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16. ABSTRACT

A Federal agency workshop to discuss a common interagency need for development of automated in situ water quality sensors was held in February 1978. The meeting was organized to focus interagency attention on the lack of adequate automated in situ devices for meeting national water quality measurement needs, and to explore possible solutions to the problem by identifying technologies that might be applied and initiating interagency cooperation to consolidate required research and development efforts.

Agency programs and academic research programs are described. Working panels addressed sensor needs and technological areas that might be applied to sensor development, including electrochemical, automated wet chemistry, optical, and electrophysical sensors. Recommendations for greater development emphasis, greater coordination within lead-agency responsibilities, and technology emphasis are presented.

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AUTOMATED IN SITU WATER QUALITY SENSOR WORKSHOP

February 14-16, 1978

cosponsored by

U.S. Environmental Protection Agency
National Oceanic and Atmospheric Administration, and
Interagency Working Group on Satellite Data Collection Systems

prepared by

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment

- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

This report addresses water quality monitoring. It presents an overview of automated water quality sensor applications, and sensor research and development activities and needs. The material presented is a compilation of prepared presentations and discussions at a U.S. Federal agency workshop. The workshop was held to provide information exchange among key representatives from these agencies on their respective automated water quality sensor programs, and to define potential areas of program coordination and co-planning in sensor research and development efforts by the Federal agency community. This information can be used not only by the Federal agencies for guidance in program planning, but by states and local governments, universities and the private sector as a similar guide in directing their research programs. The material should also be useful to those interested in a general overview of Federal sector activities in water quality measurements. For further information, contact the Monitoring Operations Division.

George B. Morgan

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas

ACKNOWLEDGEMENTS

The interest and dedication of all workshop participants should be recognized by the various agencies represented. Its success is a direct reflection of their outstanding efforts as individuals and a group.

Particular recognition goes to Ms. Barbara Pijanowski of NOAA, Mr. John Koutsandreas of EPA and Dr. Richard Paulson of the USGS and Chairman (during the workshop planning phase) of the Interagency Working Group on Satellite Data Collection Systems. Their support and initiative were the key elements in designing and conducting the workshop.

Special thanks are offered to Mr. Kenneth Birch of the Canada Centre for Inland Waters for adding a special workshop highlight by presenting a discussion of Canadian programs.

Gratitude is also expressed to the university participants for their excellent technological support. These were:

Dr. Roger Bates	University of Florida
Dr. Walter Blaedel	University of Wisconsin
Dr. Khalil Mancy	University of Michigan
Dr. F. H. Middleton	University of Rhode Island
Dr. Richard Newton	Texas A&M University
Dr. Charles Whitehurst	Louisiana State University

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INTRODUCTION

A Federal agency workshop to discuss a common interagency need for development of automated in situ water quality sensors was held on February 14-16, 1978, at the U.S. Environmental Protection Agency's Environmental Monitoring and Support Laboratory in Las Vegas, Nevada.

Sponsored by the U.S. Environmental Protection Agency (EPA), the National Oceanic and Atmospheric Administration (NOAA), and the Interagency Working Group on Satellite Data Collection Systems, the meeting was organized for two primary purposes. One was to focus interagency attention on the lack of adequate automated in situ devices for meeting national water quality measurement needs. The other was to explore possible solutions to the problem by identifying technologies that might be applied and initiating interagency cooperation to consolidate required research and development efforts.

The 3-day meeting was attended by approximately 40 selected participants, including representatives of 10 Federal agencies with water measurement programs, university scientists representing various fields of technology, and a spokesman for Canadian water programs. Several observers from industry also attended. Participating U.S. Federal agencies were the EPA, NOAA, the U.S. Geological Survey (USGS), the U.S. Department of Agriculture (USDA), the U.S. Coast Guard, the National Bureau of Standards (NBS), the U.S. Department of Energy (DOE), the U.S. Army Corps of Engineers (COE), the National Aeronautics and Space Administration (NASA), and the U.S. Navy, Office of Naval Research (ONR).

Opening session remarks were presented by Mr. George B. Morgan, Director of the hosting EPA Laboratory, and by Dr. Richard W. Paulson, representing the Interagency Working Group on Satellite Data Collection Systems. A keynote address was presented by Dr. Richard M. Dowd, Scientific Policy Advisor to the Administrator, EPA.

After a series of program presentations by agency and academic participants, the meeting was divided into five working panels, one to identify agency needs for automated in situ sensors, and four to concentrate on technological areas that might be applied to sensor development. The four technological areas of focus were: electrochemical, electrophysical, optical, and automated wet chemistry. A sixth panel, having a representative from each of the other five, met at the conclusion of the Workshop to integrate the work of the other panels and to develop overall conclusions and recommendations.

This report presents the proceedings of the Workshop. These include opening session remarks, Federal agency program narratives, a description of Canadian activities in this area, representative university technical presentations, and reports of Working Panel discussions.

SUMMARY

Seven primary programmatic findings of the Workshop participants were identified. These are summarized here.

1. There is a definite need for more emphasis on development of automated in situ sensors for water quality measurements in natural fresh and marine water bodies, in ground water, and in drinking water.

2. Capabilities exist within the present state-of-the-art to develop many of the required automated in situ sensors. Appropriate programs and funding are required to encourage such development.

3. An attractive side benefit resulting from development of in situ sensors will be the associated technology that will produce advanced automated laboratory analysis and reduce manpower requirements.

4.. There is presently little duplication of research and development efforts among Federal agencies except in specialized areas of hydrology. There is a great need, however, for better coordination between agencies, because many express interests in overlapping fields.

5. In order to define common agency needs, a general summary of national water quality data requirements was prepared and is included in the Workshop report. A more comprehensive inventory is needed and should be pursued through Workshop followup activities.

6. A steering committee should be formed to complete the work of the Workshop and to plan a second workshop within the next year to continue communication and facilitate interagency coordination. EPA and NOAA should take a joint lead in this.

7. Because of the common needs cited, research and development efforts for sensor development should be cooperative and coordinated through lead agencies. Specific recommendations have been included in the report.

In terms of technological aspects, the working panels on sensor technology considered sensor state-of-art and developments in the areas of electrochemical, electrophysical, electromagnetic, and automated wet chemical technologies. In general, all panels reported that technology exists today for improving the nation's water monitoring programs, with various levels of further development both possible and desirable. The panels felt that some of these technologies, once fully developed, could provide the States and other agencies with more cost-effective monitoring systems for water quality. The panels also concluded that selected sensors would be beneficial in laboratories when employed as rapid screening methods, reducing the time normally required by analytical methods. Such systems could also be excellent candidates for technological transfer to developing nations which may lack broad-based scientific talent and laboratories.

Of the agencies present, it appeared that the National Aeronautics and Space Administration has made significant strides towards assisting the other Federal agencies in developing the automated in situ sensor systems. A few of the automated sensor systems developed include a coliform bacteria sensor, two miniaturized multiparameter surveillance packages, and an inexpensive polarographic sensor for measuring dissolved oxygen using microelectronics.

A brief summary of the findings of each technology panel is included below.

ELECTROCHEMICAL SENSOR TECHNOLOGY

The electrochemical panel reviewed amperometric and potentiometric sensor technology. The amperometric sensors are a very valuable and versatile technique for the evaluation of water parameters. These sensors have a high capability for automated in situ measurements. They are useful with analytical techniques as detectors for liquid chromatography and in titration procedures, and have a great potential for organic analysis. The operational mode determines the response time. They are capable of detecting electroactive parameters such as: organic compounds, metals, halides, synthetic organic compounds, oxygen and chlorine, and oxygen demand. The potentiometric sensors are small and inexpensive, and can be easily adapted to automated in situ monitoring applications. They will normally require sample pretreatment, but yield good accuracy with frequent calibration. Capabilities exist for detecting selected cations and anions, including fluorides, chloride, cyanide, sulfide, calcium, coppers, cadmium and potassium, and coliform bacteria, and oxidation-reduction potential.

AUTOMATED WET CHEMICAL SENSOR TECHNOLOGY

A number of sensor technologies were considered, including ultraviolet, colorimetric, membrane electrodes, and specific ion electrodes. These would present signal processing problems for complete automation, but most are resolvable with microprocessers. A certain amount of pretreatment will always be necessary. Though high capital cost can be expected initially, a very large number of water quality parameters lends itself to detection and quantification by this technology. Automated cleaning would be necessary, often depending upon types of water. It is expected that the automatic measurements can be extended from a few hours to a few hundred hours with the application of available technology. Measurement of total dissolved phosphorus, nitrogen compounds, and dissolved total organic carbon should be pursued.

OPTICAL SENSOR TECHNOLOGY

This panel considered a number of techniques including passive and active spectroradiometry, transmissiometry, and polarimetry. These techniques do not require direct contact with the water and, as a result, require less maintenance than water contact sensors. Many of these devices use the same measurement techniques and are dependent upon electromagnetic radiation from water bodies. They can be made to scan large areas, and provide synoptic measurements. The active systems are capable of performing measurements night and day. Water parameters which can be detected include temperature, water velocity, optical properties, suspended particles, salinity, oil presence and quantity, sedimentation, turbidity, and chlorophyll-a. Spectrographic techniques could be developed to identify the more complex pollutants such as pesticides and hazardous materials. Differential radiometry can be used to measure chlorophyll concentration and turbidity. The quantification of suspended sediments and oil presence has been demonstrated by lidar polarimetry.

ELECTROPHYSICAL SENSOR TECHNOLOGY

Some of the most powerful tools discussed by this panel include acoustical and radioactivity methods. The acoustical methods can provide the thickness of oil and hazardous materials (densities less than water), and sedimentation concentration. Acoustical methods (passive) can provide information on activities of marine life, such as snapper, shrimp and schools of croakers. Radioactivity techniques include the use of neutron activation and energy dispersive x-rays. Electromechanical methods included the use of rotors and floats for measuring water velocity and tides. A measurable parameter of pollutants is specific conductance and can be determined with this technology. It has been demonstrated that solid state devices can detect thin films of oil and other pollutants with densities less than water. It was emphasized that macroscopic measurements are often overlooked but are essential to understand the large picture such as total stream flow and oil coverage.

CONCLUSIONS AND RECOMMENDATIONS

Specific conclusions and recommendations developed by the Workshop panels are listed below.

CONCLUSIONS

1. There is a great need for development of automated in situ water quality measurement systems. As suitable arrays of such sensor systems are not available, our ability to collect information necessary for adequate resource management and protection is seriously limited.

2. Due to lack of suitable sensor systems, development of other advanced measurement technology, such as satellite and aircraft remote sensing, is also limited because adequate means for obtaining supportive ground-truth (verification) information does not exist.

3. Present water quality data collection practice relies heavily on manpower-intensive methods of sample collection, analysis and automatic instrument maintenance. This provides neither real-time information nor adequate quantity and quality of data.

4. Present capabilities for data transmission, storage, retrieval, and manipulation far exceed capabilities to make accurate, reliable, real-time measurements of necessary water quality variables.

5. Automated in situ sensor systems have wide application for water quality monitoring by many agencies in fresh waters, ground water, and marine waters of the oceans and coastal zones.

6. Although Federal government agencies require water quality measurements for different purposes and in different environments, there are many areas where requirements overlap. However, the Workshop could identify little duplication in research and development efforts, except in a few specialized areas of hydrology.

7. All agencies represented at the Workshop, with the exception of NASA, have active water measurement programs. NASA

was recognized, however, to have a substantial interest and expertise in development of water measurement technology as a result of its space and aeronautical technology programs.

8. Although high-priority measurements required by most agencies could be identified, specifications required for design and development of sensing systems needed to make these measurements could not be generalized in terms of overall agency requirements.

9. Private industry research and development capabilities are considerable and, if a profitable market can be identified, industry resources can be applied to develop devices needed for automated in situ measurement.

10. Technology exists to develop many of the automated in situ sensors required. With minimum effort, short-term development could yield automated sensors to meet some requirements.

11. Interim stages of sensor development will frequently result in a number of automated devices for immediate use in the laboratory. These will reduce manpower requirements as well as the human variability inherent in manual sampling and analytical methods.

12. Automated wet chemistry sensors have high potential for short-term development success. Many techniques are already in use or have demonstrated feasibility for near-term implementation.

13. Additional high-potential technologies are acoustic and optical techniques for suspended particulate measurements, and atomic absorption spectrophotometry, neutron activation and x-ray spectroscopy for metal detection.

14. Improved in-place sensor cleaning and antifouling techniques are a high priority need to solve performance degradation by the presence of sand, sediment, and biological organisms.

15. In addition to point measurements with in situ sensors, there remains a need for mesoscale measurement schemes to obtain synoptic data over large areas.

16. Consideration of sensor development programs should include and highlight the special need for monitoring of toxic substances and hazardous materials, and efforts should be directed to meet this need whenever possible.

RECOMMENDATIONS

1. Dialogue like that initiated with this Workshop is essential and should be continued to establish national priorities, accelerate technological development, and coordinate agency efforts.

2. A similar workshop should be held approximately 6 months after publication of the first Workshop report. Coverage in this second workshop should be expanded to include areas inadequately covered in the first one (biology and radioactivity).

3. A steering committee should be formed to follow through on action items identified at the first Workshop and to plan future coordination.

4. Efforts should be made to interest one or more professional societies (e.g., Institute of Electrical and Electronics Engineers, Instrument Society of America) in including sessions devoted to in situ sensor development for water quality measurement in their future conference plans.

5. It is strongly recommended that agencies cooperate as much as possible to develop automated in situ systems for their mutual benefit through joint research and development efforts.

6. All agencies should examine their programs to identify how they can best contribute to furthering research and development efforts in the automated in situ water quality sensor field.

7. The technological expertise of NASA should be applied to address this national need for improved sensors for water monitoring systems, taking advantage of its technology transfer facilities and program. It is apparent that NASA could make substantial contributions in this area.

8. A measurement requirements survey should be formally conducted within each agency, and results of this national inventory should be published by an ad hoc Workshop followup committee.

9. An interagency briefing on the results of the first Workshop should be delivered to interested private industry representatives.

10. Consideration should be given to directing sensor research and development so interim stages of development are focused on automated analytical laboratory devices to reduce manpower requirements and the human variability inherent in manual methods.

11. The agencies outlined in Table 1 should assume lead roles in development of indicated sensors, pursuing additional funding and support, in-house and through cooperative interagency arrangements.

TABLE 1. RECOMMENDED LEAD AGENCIES FOR SENSOR DEVELOPMENT

Type of Measurement	Lead Agencies	Other Agencies With Substantial Interest
Nutrients	EPA NOAA	COE, DOE, USDA, USGS, (USDI*)
Metals and metal ions	EPA NOAA	COE, (**), DOE, NASA, USDA, USGS
Suspended particulate characterization	EPA NOAA	DOE, NASA, NOAA, USDA
Water velocity and direction	NOAA - marine water USGS - stream	COE, EPA, NBS, USDA
Petroleum hydrocarbons	USCG, EPA, NOAA	COE, (**), DOE, NASA, Navy, USGS (USDI*)
Hazardous and/or toxic material	USCG, EPA, NOAA	COE, (**), DOE, NASA, USDA, USGS
Optical properties	EPA, NOAA, USGS	NASA, Navy, NBS, USDA
Quality assurance, standards	EPA, NOAA	All

*USDI - U.S. Department of the Interior. Various elements of USDI such as National Park Service, Fish and Wildlife Service, and Bureau of Land Management may have interest.

**Other agencies such as the U.S. Public Health Service and OSHA may also have substantial interest but were not represented at the Workshop.

12. EPA should accept a lead role in development of small, automated wet chemical systems for measurement of total dissolved phosphorus, nitrogen compounds, and dissolved and total organic carbon.

13. Ongoing efforts involving optical measurement of suspended particulates should be accelerated and expanded to include existing expertise, particularly within NASA.

14. NOAA should establish a lead agency role to further evaluate existing metal ion measurement systems and accelerate development of in situ sensors.

15. All agencies should stress efforts toward development of sensor cleaning and antifouling techniques for unattended automatic sensors in natural water environments.

16. Consideration should also be given to design of systems for large-scale measurements.

OPENING REMARKS

The initial session of the Workshop consisted of opening remarks. As primary host, Mr. George B. Morgan, Director of the EPA Environmental Monitoring and Support Laboratory-Las Vegas, welcomed the Workshop participants. Dr. Richard M. Dowd, Scientific Policy Advisor to the Administrator, EPA, gave the keynote address to set the stage for subsequent Workshop discussions. Final introductory remarks were offered by Dr. Richard W. Paulson, representing the Interagency Working Group. The texts of these statements are presented on the following pages.

WELCOME

by George B. Morgan, Director
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV 89114

I'm delighted to welcome you people here to this workshop. We are honored to serve as host for, I think, a very worthwhile workshop, something that has been needed a long time.

Our fine city isn't always considered as one conducive to productivity for business affairs such as this, but we know that isn't necessarily true, particularly when we have a group of dedicated individuals such as you gathered to address a subject of great importance. I don't say that facetiously either, as I know from our experience in hosting other workshops, conferences and symposiums that groups such as this can really get down to brass tacks and do a tremendous job despite the distractions of the evening here.

You are invited here because you are honestly the key individuals from the Federal agencies and organizations that are knowledgeable about in situ water quality sensors. We have purposefully sought to keep the number of participants small for two reasons: first, to keep the group from becoming too unwieldy from sheer size, to the point of being counterproductive; and secondly to encourage participation by key personnel who are particularly qualified and interested in participating in the discussions and meeting the Workshop objectives. I believe our approach has been worthwhile. We have been gratified by the enthusiastic response and encouragement we have generally received.

In designing the workshop format, we solicited and received considerable advice and suggestions from various individuals in several agencies. The working panel chairmen, whom you will all be meeting and working with the second half of this three-day workshop, have already put in extra effort and time from their regular duties to attend a day-long planning meeting several weeks ago, and do a good deal of pre-planning homework so that we can minimize the amount of "wheel spinning" and "direction definition" normally encountered by such working panels. We're highly appreciative of the work they have already done, and for the way they have become involved to help design discussion and reporting formats.

As Mr. Wruble noted when he called the workshop to order a few minutes ago, the National Oceanic and Atmospheric Administration is a co-sponsor of this workshop. NOAA has a heavy interest in water quality sensor applications, and a keen interest in sensor improvement. The agency has been an avid supporter of this workshop. We are particularly grateful to Ms. Barbara Pijanowski of NOAA for the major effort she has put forth in planning and conduct of the workshop. She has spent many, many hours working alone and with EPA staff, including a special trip here last November for an initial planning meeting, and several meetings back in Washington since then. Her understanding of instrumentation technology and familiarity with water quality programs has been invaluable in preparing for the workshop. My personal thanks to you, Barbara, for all of your help.

The second co-sponsor of the workshop is the Interagency Working Group on Satellite Data Collection Systems. This Group has planned a similar workshop on their own, last December. When they learned of our interest in hosting a multi-agency workshop, we agreed to pool the effort and co-sponsor this gathering here at this EPA laboratory. Dr. Richard Paulson of the U.S. Geological Survey, the outgoing chairman of the Working Group, and Dr. Olin Bockes of the Department of Agriculture, the newly elected chairman have both been supportive of the workshop. Dr. Paulson will speak to you briefly regarding the Working Group's interest in sensor development a few minutes later this morning. We also had the pleasure of hosting a scheduled meeting of the Working Group here at our Laboratory yesterday.

The workshop has been designed to address a specific area of water quality monitoring--that of automated in situ water quality sensors for field applications. By that we mean contact or near-contact sensors that can operate unattended in, on or immediately adjacent to the water body being monitored, and at the field location where the measurement is desired, versus in a laboratory facility, either fixed or mobile. We are not including remote sensors, that is--those that are located at some distance, such as in an aircraft or satellite, and measure some characteristic of an emanation from the water to describe its condition or contents. Naturally, there is much more than just sensors that goes into a system to collect water quality measurements. Data recording gear, data transmission systems, data reduction facilities and procedures, equipment housing and packaging hardware, deployment and retrieval equipment, and maintenance and service requirements are some of the other factors involved. All are important, and all can be improved upon, as anything can. However, if we were to try to address all of these in a workshop such as this, it would only allow a superficial treatment of the sensor aspect. As none of the other parts in a water monitoring system are of much use unless the basic part, the sensor, is accurate and reliable, and as the sensor has the greatest need for technology improvement in the overall system package, we have chosen to devote all of the effort of this workshop on that subject. Even then, the subject is so complex, I am sure follow-on workshops, conferences or meetings will be required to keep the momentum going on the initiative of improved and more effective development efforts we hope to generate with this workshop. We are optimistic that you will give the ball an extra good shove over the next several days. It's a complex problem, but we're looking forward to your unscrambling it and identifying a route of improvement.

As a reflection of the importance EPA places on the need for improved sensors, science and technology, we are pleased to welcome Dr. Richard Dowd, Scientific Policy Advisor to the EPA Administrator, Mr. Doug Costle, and Staff Director of EPA's Science Advisory Board, as our workshop keynote speaker. Dr. Dowd has arranged to add this special side trip to Las Vegas on top of an already hectic schedule in order to be here and speak to you this morning. After a full day of work and meetings in Washington yesterday, Dr. Dowd took a late evening flight here last night, and has to leave tomorrow to present another address in Colorado. That kind of schedule can be very tiring, indeed.

Dr. Dowd graduated from Yale University and then received his Ph.D. in physics from the University of Wisconsin. He taught at Tufts University from 1965 to 1970, when he joined the Center for Environment and Man at Hartford. There, two of his program areas were:

water resource management, and
environmental affects of electric power plants.

He then joined the Department of EPA in Connecticut where he was the Assistant Commissioner for Planning and Research. In 1975 he joined the staff of the Congressional Budget Office where he was responsible for analysis of issues in the areas of general science, energy environment and natural resources.

Dr. Dowd, thank you for coming. The podium is yours.

KEYNOTE ADDRESS

by Richard M. Dowd, Ph.D.
Scientific Policy Advisor to the Administrator
U.S. Environmental Protection Agency
Washington, D.C. 20590

I am especially pleased to be here with you today, to speak with you and have this opportunity to contribute to your efforts over the next few days in this area of water quality sensor research and development. This is the first workshop, to my knowledge, that brings together the Federal agencies concerned with automated in situ water quality sensors for field applications. The success of this workshop is important to EPA and, I am sure, to the other Federal agencies concerned with environmental measurements in aquatic systems, represented here. And so, I want to lend my encouragement and support to you, for what I feel will be a very worthwhile and productive effort. I am sure that you will make it a success.

This Workshop is indeed important because the sensor itself is often the weak link in our ability to use automated water quality sensor systems. Rather recently, we at EPA received a communication from a southern Senator, urging us to expand our development of more advanced automated water quality measurement systems, stating that in his state, "Water quality is now monitored by several men carrying buckets into the marsh and taking samples. . ." He considered it an antiquated process considering our technical achievements in other areas. In contrast with this "bucket technology", about a month ago I sat in my comfortable and warm living room watching the Super Bowl, played in the Super Dome, located not far from the area the Senator referred to. I agree, and I am sure you agree with the Senator, that bucket-dipping technology is antiquated in contrast with the technology which allowed me to view that game first hand.

Why do we need sensor systems, and reliable sensors as part of those systems? There are a number of reasons for collecting water quality measurements. Legislative mandates alone place a large burden of data collection upon us.

It is sobering to try to list the research and monitoring needs associated with such recent Federal legislation as the Federal Water Pollution Control Act Amendments, the Ocean Dumping Act, the Deep Water Port Act of 1974, the Toxic Substances Act, the Marine Protection Research and Substances Act of 1972, the National Environmental Policy Act of 1969, the Coastal Zone Management Act, the Safe Drinking Water Act, and the Federal Environmental Pesticide Control Act of 1972, to mention a few. All have spawned a tremendous need for more advanced and sophisticated technology for water quality measurement. One purpose of this conference is to lend impetus to the research and development of automated sensing techniques to keep pace with the need for such technology.

The era we are now living in necessitates that we have better quality and quantity of measurements on which to base legislation and policy and our judicial enforcement. No longer can we go out and casually look at a river, conclude it is polluted because it looks bad to us, and expect something to be done about it. We must have quality measurements if some meaningful action is to be taken to improve the water quality of the river. As our measurements become more and more sensitive, we seem to find more and more environmental contamination. Likewise, the distribution of old and new contaminations seem to be more and more widespread in aquatic systems. To address these environmental problems, we need more and better measurements.

In this context, of course, we are sometimes driven to a "bucket dipping" technology, as our needs quickly outrun our ability to instrument for field use. A theme I would like for you to keep in mind during your discussions is the need for tieing the human into whatever sensor system is used. By this, I mean you must assess implementation possibilities in terms of simplicity, timeliness and cost (capital versus labor), simplicity of operation, timeliness of results and cost of introduction of the technology. It is on these grounds that new technologies are often proven good or bad.

The need for water quality measurements is increasing exponentially, while the manpower and money available to us to make these measurements are increasing at a much lower rate or, in many instances, not increasing at all. The only solution is improved technology to make these measurements. We at EPA--and I am sure we are not unique among the Federal agencies--just don't have the manpower and money to use the bucket-dipping technique to make all the water quality measurements be valid and accurate enough to stand up in court or to warrant a major expenditure of funds for cleanup and control. If we did have the money and people, would we want to do it this way? I doubt it.

Additionally, I think we have all found ourselves frequently frustrated and hampered by our inability to make the broad spectrum of parametric measurements so often needed to classify or characterize water. Science and technology alike depend on the ability to measure an enormous variety of phenomena. Without instruments to make such measurements there can be no efficient analysis and prediction.

Another problem area we face is limitations associated with the episodic movement of nutrients and other pollutants require either enormous short-term investments in manpower or advanced sensor technology capable of making the necessary synoptic or near-synoptic measurements. Increasing manpower to meet such situations is usually impossible or impractical. We are, therefore, highly dependent upon advances in the state of the art to provide more rapid and more precise sampling and sensing techniques capable of detecting a broad range of environmental pollutants at or below environmentally significant levels.

In the past, we have tended to rely on measurements which were either easily or dependably made or which, through extensive labor in the analytical chemistry laboratory, yielded values sensitive enough to be environmentally meaningful. The series of operations involved includes sampling, storage, chemical analysis, key punch and data entry, and requires prolonged time periods incompatible with many of our information needs. Hopefully, equipped with an armamentarium of automated sensors, tomorrow's scientists will be able to select those parameters for measurement which can best provide the answers to our monitoring questions in time frames required for remedial actions.

Everyone who has had experience with automated water quality sensors under field conditions can testify to problems concerning fouling, sensitivity, range, hysteresis, calibration, non-linear drift, response time, precision, accuracy, and interferences. Coupled with this is the fact that many of the sensors available are too delicate for field conditions, if there even is a sensor available to measure those parameters we need. It makes one wonder if we have really advanced significantly beyond bucket-dipping techniques.

Previously, I stated that the sensor itself is often the weak link in automated water quality monitoring systems. The technology needed to deploy such systems involves transportation, communication, data storage and handling, packaging and sensing. A society which can send a man to the moon and back certainly has the capability to deploy and retrieve packages. The technology which allows us to communicate with ships and men under the sea certainly allows us to communicate with monitoring packages. The techniques which allow us to take a census of 230 million people in the United States and store, manipulate, and summarize the information, certainly allow us to store and manipulate the data from water monitoring packages. The technique which allows us to package instruments to withstand a harsh Martian environment certainly allows us to package instruments to withstand aquatic environments on Earth. We certainly also have the capability for the research and development needed to adapt and make these technologies economical for our use.

Today a new generation of powerful measuring instruments is beginning to emerge, and we must capitalize on it. Not only do we need new and improved sensors, but we might take a lead from a recent advancement in chemical analysis procedures that employs a combination of two instruments; for example, the gas chromatograph and the infrared spectrometer. The combination is a powerful analytical tool. We might examine this to see if some similar approach of sensor paring can be of utility in sensor technology improvements. Additionally, adaptation of advanced systems such as the X-ray spectrometry package NASA used aboard the Viking lander for determining heavy metal constituents in Mars soil might well be possible for incorporating into automated waterborne systems for deployment in lakes, streams and other water bodies. If measurement limits can be lowered for use in water systems, this could be a real boon to many of us. Another recent technology advancement involves a small, inexpensive oil sensor using a specific heat principle. This may answer many of our needs for monitoring water areas susceptible to oil contamination. There are other new ideas and prototypes being pursued by government, academic and industrial groups. Each of you here is familiar with these various effects, and these ideas and possibilities need to be shared and explored. The "two heads is better than one" philosophy still applies.

A fundamental goal of this workshop is to establish more communications and interplay in the Federal agency community to orchestrate our efforts in this technology area. This interchange needs to take place among the agencies as well as with others working on trying to improve our technology, such as by the academic institutions represented here today by members of several leading universities.

Leadership in Federal agency program planning and technology development will have to come from you. I am sure I tell you nothing you aren't already aware of, but you do face a challenge in using this workshop, and managing your various programs, to more effectively deal with the overall challenge - that of carrying out the most effective program possible to respond to the sensor improvement needs I have outlined.

It has been noted that EPA has a particular interest in incorporating a variety of sensors into small, reliable automated waterborne monitoring packages. Mr. Morgan, the Laboratory Director here, has told me that in dealing with others interested in water measurements, he and his staff have regularly encountered the problem of trying to keep up with the numerous activities and new developments in sensor research and development. That experience, coupled with the recognition and pursuit of an improved research and development effort in this area by Mr. John Koutsandreas and others in the EPA Office of Research and Development, led to the genesis of this Workshop.

Based on this background, I wish to charge you with the workshop responsibilities of:

Reviewing Federal Agency water quality sensor applications and research and development activites.

Identifying commonalities and overlaps in research and development activities.

Identifying research and development gaps.

Identifying possible cooperative research and development efforts, and

Developing recommendations for future research and development directions.

In reviewing the list of participants and the agenda, I am indeed impressed by the caliber and breadth of experience this Workshop has been able to assemble here. Such representation is essential to meet the charges and challenges which I have laid before you. Congratulations are in order to the organizers of this workshop for their excellent job. And to you, the participants, I wish you success in your deliberations and my sincere appreciation for your willingness to take on this job, vital to all of us.

And let me add one final note to your discussions - do not forget the human element. Tailor the response to the need. There may be situations that one can conceive where you require such a flexible system that only "bucket dipping," backed up by an analytical laboratory will suffice.

There are many things we can do for water quality measurement in terms of reliability timeliness, costs and parameters with automated sensors. They cannot, however, solve all the problems, at all times.

Tnank you and good luck.

INTRODUCTORY REMARKS

by Richard W. Paulson, Ph.D.
Interagency Working Group on Satellite Data Collection Systems

I'd like to just make a few brief remarks about our Interagency Working Group and why we very heartedly support this particular workshop.

For several years a number of Federal agencies have been testing a new technology called "Satellite Data Collection Systems," which is basically a fairly straightforward technology from the user's point of view, whereby one can telemeter data from in situ sensors. The community of individuals within these agencies is rather small.

About two years ago we formally banded together and formed this Interagency Working Group on Satellite Data Collection Systems, and we meet about once a month. Our objective is basically to keep each other informed on our activities in this technology.

It is a rather well-developed technology, and we all are very optimistic that we can use it operationally here in the coming years. What has become rather clear to us very quickly is that the weak link in the chain is the sensor.

We have existing satellite telemetry systems in orbit now that would allow us to put a small battery-operated radio on the roof of this building and, several times a day, telemeter all the data that a water quality sensor would produce through that satellite back to some central receiving station where we could process it and analyze it and all the rest. But really the weak link is that sensor, and last year we began to discuss the possibility of dedicating one of our monthly meetings to just this area-- water quality sensors. We were informally going to get together and tell each what our various agencies were doing. And concurrently John and Don were laying the groundwork for this Workshop. And since so much of what they wanted to do was what we wanted to do, we decided rather than holding two such meetings, we would join forces and try to cosponsor this one.

So we look forward to a very successful meeting. We have representatives from the Department of Agriculture, Department of Energy, NASA, NOAA, Corps of Engineers, representatives of the DOD and the Geological Survey, representatives of the Department of Interior and EPA. We put out a newsletter every 2-3 months and if you are interested in the technology, talk to me and we can get you on the mailing list for this publication.

I think what we are trying to do here today and in the next few days is communicate with each other. So, in summary, we appreciate the opportunity to join in this workshop and we're going to do what we can to help make it a success.

Thank you!

FEDERAL AGENCY PROGRAMS

Prior to the Workshop, each participating Federal agency was requested to prepare a written narrative describing its programs in automated water quality sensor applications, needs and/or research and development activities. Each was asked to address such topics as why the agency is interested in water quality measurements (legislative requirements, etc.), what sensor applications are in use, where sensors are geographically employed, the kind of environment(s) the sensors are employed in, parameters of interest, measurement sensitivities desired, present sensor deficiencies, existing and future sensor requirements, technology forecast (i.e, what promising or potential technology is seen), views on interagency coordination of sensor research and development, and the gap-filling and duplication of effort and problem solutions they see. The narratives thus prepared are presented on the following pages.

In addition to the written material, each agency was requested to present a 20-minute oral summary of its programs as described in the narrativebylines, and on the Workshop agenda at the end of this report.

U.S. ENVIRONMENTAL PROTECTION AGENCY

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The Office of Water and Hazardous Materials is involved in several water quality-related activities and therefore, has a variety of related water quality data needs.

For example, we need statistically sound and defensible data to support the development of effluent guidelines for setting NPDES permit conditions. This involves collecting samples in and around various industries to determine the types and amounts of pollutants in their effluents and incorporating this information into a technology-based review of in-plant processes. The end product is a set of effluent guidelines for the different industrial categories.

Whereas in the past effluent guidelines were more oriented to such classical parameters as suspended solids, biochemical oxygen demand and pH, we now have a need for data to support the development of best available technology guidelines necessary to control the discharge of the 129 toxic compounds identified in the National Resources Defense Council (NRDC)/EPA Settlement Agreement. We also have a need for data to determine if any additional toxic compounds are a problem and therefore should be controlled through the effluent guidelines process. This agreement not only requires that the EPA set effluent limitations for these toxic compounds, but also requires that the EPA monitor to determine if these BAT limitations are adequate. The requirements of this agreement have now been incorporated into the most recent Amendments to Public Law 92-500.

On the other end of this process, once permits are in force, we need data to determine whether a facility is in compliance with its permit conditions. This is usually accomplished through on-site visits or as part of an intensive survey.

We need data to conduct those analyses that are necessary to answer legislative questions, such as: Are national water quality conditions improving or getting worse? Are abatement/control programs working? Are State water quality standards adequate to allow for the protection and propagation of a balanced population of fish, shellfish, and wildlife? This requires that a well-rounded data base which is up to date with current legislative issues and concerns be maintained. This also involves extensive monitoring. We have a special need for more information on toxic substances. We need data to evaluate long term potential effects from toxics.

We need data for planning purposes in designated and statewide planning areas to support the preparation, adoption and revision of water quality management plans and the establishment and implementation of regulatory programs identified in these plans. Under 40CFR Parts 130/131, State and areawide planners must conduct water quality assessments, and then develop effective pollution controls based on these assessments. The majority of these water quality assessments should be based upon intensive surveys. We have a special need for more reliable nonpoint-source related data in support of this planning process.

We also need data to support the drinking water program, especially data on ambient raw water quality and groundwater quality. We have a special need for more toxics data around water supply intakes to determine which chemical substances are present and in what amounts.

The EPA Regions and States, principally through the Section 106 grant process, provide most of the information needed to satisfy these various needs. EPA Headquarters and other federal agencies provide the remainder principally through special studies and such long-term ambient monitoring networks as the EPA National Water Quality Surveillance System (NWQSS) and the USGS National Stream Quality Accounting Network (NASQAN). Each year, the Office of Water and Hazardous Materials works with the Regions and States through the annual program guidance process to ensure that State/Regional monitoring activities reflect changing as well as current program emphases.

In the past, most federal, Regional and State monitoring activities conducted to support these needs were limited to collecting water samples at ambient fixed stations and analyzing them for such classical water constituents as dissolved oxygen, pH, BOD_5, suspended solids, fecal coliform and so forth. These stations were usually visited on a routine basis, and monitoring activities generally were geared to providing water quality trends, establishing water quality/land use relationships, and supporting other very basic analyses. Monitoring for the more exotic compounds was limited due primarily to resource and technological constraints, although some very basic toxics information, especially heavy metals information, was collected. Any additional toxics information was usually gathered through special studies.

Today, however, monitoring is changing very rapidly. Now that NPDES permits are in force and construction activities are well underway, monitoring is taking on new directions. In 1976 and 1977, a special Standing Work Group on Water Monitoring, operating within the office of the EPA Deputy Administrator, worked with the Regions and States to develop a Basic Water Monitoring Program. This program is designed to: Redirect ambient and effluent monitoring at the State level from a fixed station single discharge approach to an intensive survey approach; Identify dischargers to the State's waters and assess their water quality impact; Define a minimum number of fixed ambient stations for national use that will be operated at the State level within a consistent framework; Provide a coordinated nationwide assessment of selected toxic compounds; and, Ensure that data which are collected are not only used in the decision-making process, but are also used to educate the public and inform the Congress.

Under this program, goals have been set for the operating level of intensive surveys by the States. The goal is to conduct an intensive survey at least once within 5 years on every river, lake, estuary, bay or aquifer where wasteloads are allocated, or significant water quality changes either have been identified or are considered probable.

Under this program, goals have also been set for the operating level of ambient fixed stations selected as part of the Basic Program. The ambient stations will be operated by the State. Data will be aggregated nationally and will be used primarily to determine national trends in water use areas such as water supply, fishing/shellfishing areas, etc., and in problem areas, land use areas and in areas where future development may impact water quality and thus baseline trends are needed.

Finally, goals have been set for the operating level of effluent monitoring programs. Major dischargers will be inspected annually with sampling as necessary to ensure compliance with applicable effluent limitations.

This Basic Program is intended to serve as a set of monitoring guidelines under the Section 106 Appendix A regulations and is currently being implemented by the States.

In addition to the changes brought about by the Basic Water Monitoring Program, the EPA's monitoring emphases are also expanding in the area of toxic pollutants. In response to the NRDC/EPA Settlement Agreement and now the new Federal legislative amendments to PL92-500 (Clean Water Act of 1977), the Office of Water and Hazardous Materials is actively involved in collecting samples for toxics analysis. During 1978, the EPA Regions, in cooperation with EPA contractors, will be collecting some 2,000 samples nationwide and will analyze them for the 129 toxic compounds identified in the NRDC/EPA Settlement Agreement. These samples will be collected from effluents, ambient water, water supply intakes, sediments and tissues. The resulting data will then be used to support exposure/risk studies, fate and distribution assessments, and other general studies.

An additional several thousand samples will be collected under contract in 1978 and analyzed for these toxic compounds in support of the effluent guidelines development process. The EPA will also expand its toxics monitoring program to other areas such as sludge. Toxics monitoring not only holds a high agency priority but is also a continuing program that will expand over time.

Finally, the Clean Water Act of 1977 requires that we expand our monitoring activities to include not only the 129 toxics which I have mentioned, but also additional toxics and what the law calls nonconventional pollutants. These are constituents that have not been designated as either toxic or conventional (BOD, suspended solids, etc.) but must, nevertheless, be controlled under BAT effluent limitations.

As you can see, monitoring especially in the toxics area, is evolving quite rapidly. We are moving away from the routine monitoring of the classical parameters at several fixed stations to the monitoring of toxics and the conduct of intensive surveys. If technological support is to keep pace, it must also evolve rapidly.

One of the reasons for holding this workshop is to find ways of strengthening current water quality sensor technology. This is all well and good. For example, we need to strengthen the reliability of existing in situ water quality sensors to gather more reliable real time information on nonpoint-source related pollution. For our purposes, I feel that efforts must be made in this area. But, more importantly, I strongly suggest that if we are to keep up technologically with the monitoring process, we must stay one step ahead and concentrate our efforts on developing new water sensors to detect toxic compounds.

We are looking for a way to reduce the high costs of toxic analyses. For, the analytical costs involved in toxics monitoring are high. Typically, it costs anywhere from $800-$1,500 to analyze one sample for the 129 toxic compounds. Multiply these costs times the several thousand samples required to adequately support the program and you have a very expensive program.

We need a low cost, reliable method--and I emphasize low cost and reliable--to detect and quantify, in the water column and effluents, the 129 toxic compounds identified in the Settlement Agreement. We need this not only to round out our data base on these toxic compounds while saving resources in the laboratory, but also to strengthen the regulatory arm of the Agency.

Over the last several months we have investigated the use of various in situ bioassays and also an immobilized enzyme technique as potential means of gathering reliable toxics data while reducing the costs of toxic analysis. In this connection, a water quality sensor may be available, or could be developed to satisfy this need. In any case, the time is ripe to start looking at some of these new techniques.

Now, I am not suggesting that we immediately go out and develop an in situ water quality sensor for each of the 129 toxic compounds. But I do suggest that we develop, minimally, a sensor or series of sensors, sensitive to the parts-per-billion (ppb) level, that could serve as a screening device to tell us if a particular class of toxic compounds is present or not. The general classes under which the 129 toxic compounds are grouped include halogenated hydrocarbons, the pesticides/insecticides group, heavy metals, the aromatics, industrial solvents, the phenols, the benzene toluene group and miscellaneous compounds. A screening method such as this could result in considerable savings in the laboratory.

It would also be desirable if this sensor or series of sensors indicated relative concentrations or magnitudes of toxicity. Then, as technology evolves, perhaps these sensors could be redesigned to be more quantitative than qualitative in nature.

Water samples currently being collected by the EPA Regions and contractors could possibly be split and made available through the EPA Office of Research and Development to check the performance and reliability of these sensors as they are developed.

If we had a low-cost and reliable in situ water quality sensor designed to detect classes of toxic compounds we could:

- free up valuable resources in the laboratory to support other high priority activities;
- develop an early warning system for industry or field use that could help prevent or at least allow us to respond more quickly to accidental toxic spills;
- establish the sensor(s) in privately owned treatment works (POTWs) to determine the correct retention time for most effective treatment;
- measure the impact of the volatile toxic compounds on the receiving waters more effectively; and,
- measure the variability and frequency of toxic discharges more effectively.

We could do a great deal with such a sensor and the Office of Water and Hazardous Materials is willing to cooperate with the

EPA Office of Research and Development and the scientific community to develop it.

In conclusion, let me leave you with this one word of caution. I think the challenge of developing such a valuable in situ water quality sensor is attractive. But, the real challenge is to make sure that it is reliable and cost-effective. Let us, therefore, work toward this goal.

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

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Unlike some of the other agencies represented at this workshop, the National Oceanic and Atmospheric Administration is a relative newcomer to the federal system. Along with the Environmental Protection Agency, NOAA was created under a presidential reorganization order. Unlike EPA, however, NOAA was not given independent agency status, but was placed under the Department of Commerce. NOAA is the only federal agency with general ocean responsibilities; the purpose for its creation was to consolidate federal civilian ocean activities so that improved coordination would lead to more effective and efficient ocean efforts.

NOAA has three primary goals, ocean resource management, coastal zone management, and environmental surveying, monitoring, prediction and control. The atmospheric activities of NOAA are considerable and until the past few years, NOAA's efforts in environmental monitoring and prediction have concentrated primarily on the atmosphere rather than the ocean.

NOAA's overall responsibilities related to its ocean functions can be stated in general terms as:

- assessment of ocean resources including living resources and minerals, but excluding hydrocarbons;
- execution of research leading to an understanding of the naturally occurring phenomena in the marine environment, and;
- execution of research leading to an understanding of the distribution, fate, amd effects on marine ecosystems, of pollution and disturbances caused by man, and coastal surveys for mapping, charting and geodesy.

In order to carry out such responsibilities comprehensive programs are required for the integration of basic research, baseline studies and monitoring operations in estuaries, on the continental shelf, in the deep oceans and in the Great Lakes. NOAA's requirements for water measurements therefore span the entire range from fresh water to sea water in depths ranging from the top few centimeters at the air-sea interface to shallow bays and the deep ocean. In addition, measurements must be made from stationary platforms such as buoys and towers, from moving platforms such as ships and helicopters with towed devices for profiling apparatus, and from remote platforms such as aircraft and satellites. NOAA has a need to obtain synoptic measurements over wide geographical areas in order to examine the big picture, as well as microscale measurements over a few centimeters in order to observe the microstructure of an individual patch of plankton or chlorophyll.

Measurements are made at the air-sea interface, in the water column, and in the particulate matter in the water column; in the sediments on the bottom and in the interstitial waters of these sediments as well as in the biological organisms that swim and drift through the water column or crawl, burrow, or attach themselves to the ocean floor.

Since this workshop is concerned primarily with the measurement of water quality, it would be useful at this point to differentiate between water quality measurements and those typically thought to be oceanographic measurements. Water quality measurements provide an understanding of the water environment and its ecosystems that can be used for assessing the character of the water system and determining the effect of man-induced disturbances. Water quality measurements are (1) those that quantify actual pollutants such as hydrocarbons and metals; (2) the chemical and biological parameters that characterize the environment in which the ecosystem exists such as totalorganic carbon and nutrients; and (3) general supportive measurements that lead to information on the distribution and dispersion of pollutants. Supportive measurements are generally currents, temperature, salinity and, at times, waves and tides.

It is important also to recognize that there is a close relationship between water quality information and fishery assessment information. Both kinds of information are necessary for assessing the impact of pollution on the environment and for understanding the natural relationships between fisheries and the environment. Because of our present lack of knowledge concerning these interrelationships and our lack of adequate measurement technology for pollution studies, it is often necessary to use biological organisms themselves and their abundance and distribution data as indicators of water quality. It is not possible therefore, to treat fishery assessment activities independent of water quality assessment activities.

Most of NOAA's water measurements result from requirements of several programs which have evolved historically to carry out functions that were inherited from NOAA's predecessors and to respond to more recently legislated responsibilities such as the Marine Protection, Research and Sanctuaries Act of 1972 and Fisheries Conservation and Management Act of 1976.

NOAA's programs are broad in scope and require the collection, storage and utilization of data on many levels. Data are collected through various programs by NOAA's own survey activities and through the use of contractors. NOAA presently has 24 ships, 14 of which could be used for collecting oceanographic and fisheries information; however, most of NOAA's water quality data are collected under contract by university and private industry groups. NOAA stores and manages marine environmental data through its National Oceanographic Data Center which is part of the Environmental Data Service. And finally, NOAA uses the information that it collects and stores to assess and predict environmental and resource conditions for management decisions by NOAA, EPA, and the Department of Commerce.

Most of NOAA's current water measurement activities are carried out through five major programs; several additional programs are still in development phases, and some limited measurements are made as part of other general research activities. A short description of each of the major programs follows:

Marine Resources Monitoring Assessment and Prediction Program

(MARMAP) MARMAP is designed to provide the necessary information for management and allocation of the nation's marine fishery resources. The program is long term and requires the collection and analysis of data to provide basic information on the natural abundance, composition, location and condition of the commercial and recreational marine fishery resources of the United States.

Ocean Pulse

Ocean pulse is a new program whose objective is to monitor the "health" of the ocean or the consequences of pollution on living resources. The program is designed to provide baseline information on physiological and biochemical parameters of indicator species as well as basic water quality information at specific sites in order to assess the health of the living resources. The initial study area is the continental shelf off the northeast coast of the United States.

Marine Ecosystems Analysis Program

(MESA) MESA is designed as a NOAA program to focus the cooperative efforts of federal, state and local agencies, universities, industry and environmental organizations on the investigation of specific marine environmental problems within limited geographical areas. Selected coastal and offshore areas are subjected to intensive investigation for relatively short periods of time (5-7 years) to determine the impact of man on the ecosystem of the areas and to gather sufficient information to be able to predict consequences of future activities there. The area selected for the first MESA project which began in 1972 was the New York Bight. The Bight is adjacent to one of the most populated and industrialized regions in the world. It is a repository for wastes from over twenty million people and a host of major industries as well as the recipient of the nation's largest ocean dumping operation. Additionally, the area is an important environmental resource, with abundant commercial and recreational fisheries. The second MESA project was started in 1975 in Puget Sound. This area, unlike the New York Bight, has no evident large-scale environmental problems at the present time and study of the area is expected to provide information that will lessen the impact of the increasing stresses associated with economic growth and industrial expansion that are now taking place. Additional areas may be added to the MESA program in the future.

Ocean Dumping Program

This was established as a direct result of legislated responsibilities. Under Title II of the Marine Protection, Research and Sanctuaries Act of 1972, NOAA was given responsibility for conducting research and monitoring the environmental effects of ocean dumping. The program is a continuing one and its objectives are:

- determining the environmental effects of past and present dumping activities
- investigating proposed new dump sites
- monitoring selected dump sites
- supportive laboratory and field studies to investigate pathways and fate of dumped materials
- developing dump site selection criteria and criteria for differentiation between harmful and non-harmful materials for dumping.

The Deep Ocean Mining Environmental Study

(DOMES) Domes is a program concerned with the environmental problems that may arise from the deep-ocean mining of manganese nodules. The objectives of the program are to:

- identify potential environmental problem areas and establish priorities for research,
- obtain baseline information for potential mining areas,
- develop and test predictive models for the effect of ocean mining on the marine environment.

One unique aspect of this program is that this is the first opportunity for observation of environmental consequences of a new industry from the beginning. Since deep ocean mining has not yet progressed beyond experimental stages, opportunity to establish true baseline information as well as to observe first hand the effect of mining operations on the environment.

The Outer Continental Shelf Environmental Assessment Program

(OCSEAP) OCSEAP as coordinated by NOAA is concerned with the outer continental shelf of Alaska. It has as its primary objective collection of the information necessary to enable protection of the marine environment in that area in a manner that is compatible with offshore oil and gas development. The program is being conducted by NOAA for the Department of Interior's Bureau of Land Management. It focuses on nine lease areas on the Alaskan outer continental shelf. General objectives of the program are:

- location of critical wildlife habitats that must be protected
- prediction of effects of oil and gas spills or other disturbances generated as a result of the oil and gas development
- identification and development of new monitoring techniques
- definition of environmental stresses on manmade structures in order to reduce polluting and safety incidents.

Hazardous Materials Response Program

Although this program has not been fully implemented within NOAA, some efforts have been initiated during the past year. It is designed to provide quick response to oil spills so that required data on the fate and behavior of oil can be collected in order to improve modeling efforts for forecasting and prediction of the movement of spilled oil in the marine environment. The objectives of the program are to:

- provide on-scene support to Coast Guard coordinators with respect to clean-up, containment and mitigation of impact
- provide damage assessment
- perform research on actual spills

At the present time, this program does not have its own staff, but draws experts from other water programs in-house as needed for specific projects.

Although each of these water programs is run separately and from different organizational levels within the agency, many common elements exist, particularly with respect to requirements for data acquisition. Appendix 1 is a listing of parameters which to one degree or another have been identified to be of interest in NOAA programs.

Appendix 2 provides information on measurement requirements for nine of the most commonly measured parameters as they were identified in a 1976 workshop (1). Although this information was gathered from many non-NOAA sources, it is typical of all water quality requirements. It is not surprising to find that most of these parameters also happen to be the only ones for which direct measuring in situ instrumentation for use in sea water is readily available.

Although some NOAA programs have been able to provide detailed requirements for a few of the most commonly measured parameters, program managers have been unable or unwilling to document specific requirements because:

- The research nature of some projects makes it difficult to predict expected conditions during the program planning stages in anything more than general terms;
- Most programs have only minimum lead time and must begin operations immediately with very limited budgets, i.e. short term high visibility programs are the rule rather than the exception. The luxury of lengthy and expensive development programs for new or improved measurement techniques to satisfy requirements for better accuracy and reliability cannot be afforded. Consequently, program managers tend to settle for the available technology and specify their requirements in terms of what they know the available equipment can provide.

To add more complexity to the situation, actual measurements for many programs are taken by activities under contract to NOAA. Many of these contractors have their own equipment and capabilities which may result in compromises between the requirements that are actually desired by the program planners and those that are realistically possible had their budget provided for procurement or development of more advanced and reliable equipment.

In general terms, the deficiencies that persist in marine water quality measurement technology fall into two categories: those systems that exist and need improvement, and those systems that do not exist at all. Under the first category, systems do exist for the in situ and/or near real time measurement of temperature, salinity/conductivity, depth, dissolved oxygen, pH, current speed and direction, optical properties and chlorophyll a, in marine waters. A few additional parameters can be measured in fresh water because of fewer chemical interferences and different concentration range . Of these systems, only those that measure temperature, salinity/conductivity and depth can be considered to be adequate, i.e., fairly reliable measurements can be achieved with current state-of-the-art instrumentation. All of the other measurements can be achieved to lesser degrees of reliability. Current measuring instruments are not standardized and different current measuring techniques produce different data in dynamic environments. Dissolved oxygen and pH systems are unsuitable for long term unattended use because of their calibration instability and frequent maintenance requirements. The measurement of optical properties and chlorophyll is complicated by the wide variety of devices available for measurement with little comparability as well as problems with fouling during long term unattended use. In all cases, the limiting factor in these systems is the sensors and not the electronic or data handling components.

As far as the need for new sensors is concerned under the second category, a brief glance at Appendx A will illustrate that out of that entire list, only a handful of parameters, those listed under the first category, can be evaluated outside of a controlled laboratory environment. In order to make these measurements, analysis must be performed using standard wet chemical techniques on samples that have been laboriously collected at a few discrete points and have been removed from their surrounding environment, artificially preserved, aged, and subjected to numerous sources of contamination, yielding far less than real time or synoptic information.

Sensors simply do not exist for most of the parameters of interest in marine waters. While it is neither practical nor desirable to develop in situ measurement techniques for all of the parameters listed in Appendix 1, it is necessary to develop such systems for the parameters that must be:

- measured frequently, or
- measured in remote or inaccessible areas or areas where the cost of sending a man to obtain the measurement is very high (operating costs for an oceanographic vessel are in the neighborhood of $4000 per day), or
- measured precisely, subject to fewer of the variations and uncertainties caused by individual analysts.

Recommendations

NOAA has produced several documents that consider water quality measurement recommendations. "Marine Pollution Monitoring: Strategies for a National Program" (2) is the product of a workshop sponsored by NOAA in 1972. At that time the contaminants of greatest concern were identified as heavy metals, petroleum and halogenated hydrocarbons. Since that time additional categories have been added (3), namely low molecular weight halocarbons and transuranic elements.

In addition to the requirements that have been identified above, personal contacts and interviews with key program personnel in NOAA have identified several additional areas where improved technology for in situ measurement would be desirable. Priorities have not yet been evaluated.

Needs have been identified for:

- water clarity measurements over the entire water column
  - available light to biota at selected depths,
  - characterization of particulates in order to distinguish between natural particles and particles of dumped material,
  - ability to track dumped material
- in situ ammonia measurement in the water column and near the bottom (to 1 Mgm/l level)
- continuous and periodic measurement of heavy metals and associated speciation
- measurement of total available nitrogen, i.e., nitrogen in forms available to the biota (unfortunately this varies with the organisms)
- measurement of sulfides in sediment
- measurement of total organic carbon in dissolved and particulate forms
- measurement of total biomass
- measurement of chlorophyll to map plankton patches, (locate chlorophyll maxima and obtain time and spatial variations)
- measurement of plankton over large areas
  - phytoplankton: identification of algae type
  - zooplankton: identification of species and size distribution
  - zooplankton: particle count and volume
- reliable dissolved oxygen sensors for long term unattended use
- closer to real time data on nutrients.

In the past, NOAA's efforts in the research and development of in situ water quality devices have been limited to areas of overlap with traditional oceanographic programs.

1. The Office of Marine Technology in the National Ocean Survey has been exploring an acoustic technique for the underway shipboard measurement of water currents. This project was begun in FY 76 and is scheduled for completion in FY 80.

2. Initial research efforts by Dr. Donald Barrick of the Wave Propagation Laboratory of NOAA have demonstrated the feasibility of using shore based high frequency radar to provide a map of surface ocean currents

to a distance up to 50 miles from shore. The possibility exists for extending the technique to include directional wave measurements. The Office of Ocean Engineering will be working with the Wave Propagation Laboratory to carry out the engineering development necessary to provide a commercially available system.

3. An attempt to produce a more reliable and accurate dissolved oxygen sensor for use as a laboratory standard has led to considerable research on the polarographic dissolved oxygen probe by Dr. J.A. Llewellyn of the University of South Florida. His work sponsored by NOAA has produced a great deal of information on the limitations of polarographic techniques for dissolved oxygen measurement.

4. For the past several years, Dr. John Proni of NOAA's Environmental Research Laboratory in Miami, has been experimenting with towed echo sounding systems for the acoustic measurement of suspended sediment in water. Using a 200 KHz signal, he has been able to track sediment and sewage sludge plumes and estimate suspended load throughout the water column. Using 3 MHg signals, estimates of sediment load per centimeter near the bottom and mixing rates have been obtained. The system is still a research tool, and work is continuing on its improvement.

Research and Development Programs

The responsibility for improving measurement technology within NOAA falls within the Office of Ocean Engineering. This office was formed a little more than a year ago to serve all of NOAA as a focal point for ocean technology development. One of the major programs within the office deals with development of ocean instrumentation. In order to provide direction to this program, several studies are being conducted which assess the water quality measurement and standards needs of NOAA and the marine community. The measurement needs assessment study is being carried out by MAR Inc., Rockville, MD, under contract to the Office of Ocean Engineering; preliminary reports are available now and a final report is due at the end of this month. Several additional contracts dealing with marine water quality standards and quality assurance programs are also underway.

Beginning this year, FY 78, the Office of Ocean Engineering will be funding additional efforts in water quality measurement R&D. In addition to the technology assessment programs mentioned earlier which are needed to give direction to the program, the FY 78 program includes the following projects, all of which will be carried out under contract to the OOE:

1. improvement of dissolved oxygen sensors for long term unattended use,
2. improvement of current measurements with existing instrumentation,
3. engineering development of the HF radar system for surface current measurement,
4. improvement of standards for conductivity and current measurements.

The FY 79 program for which $620K has been requested in the President's budget, includes additional efforts for:

1. development of field standards for chlorophyll and dissolved oxygen,
2. initiation of a program for automation of plankton classification and counting,
3. evaluation of existing oil slick sensors for use on unattended buoys.

Projected plans for the FY 80 program will require about a fourfold increase in the budget and includes additional efforts for:

1. development of an ammonia measurement system for in situ, real time use
2. development of in situ techniques for measurement of trace elements and speciation
3. improvement of underwater light measurements
4. development of in situ measurement system for suspended particle characterization.

Interagency Cooperation

NOAA's only formal cooperative efforts in water quality measurement at the present time are with the Environmental Protection Agency with Energy Pass-Through Funds, and the National Bureau of Standards. Both efforts involve the development of laboratory and field standards. The programs deal primarily with standards and procedures leading to improved data quality, and not toward the development of in situ instrumentation.

While no formal cooperative agreements with other federal agencies exist, we have followed with interest the R&D being carried out by NASA-Langley, in the measurement of chlorophyll and coliform, and the USGS in their improvement of suspended particle/turbidity measurements.

At the present time, within the federal system, we cannot identify any areas of R&D overlap for development of in situ measurement techniques. We can however identify many gaps, most of which have been pointed out earlier in this presentation.

References

1. "Measurement Requirements for Marine Water Quality Data," B. Pijanowski, Oceans '76, Sept. 1976

2. "Marine Pollution Monitoring: Strategies for a National Program," ed. E.D. Goldberg, NOAA, Oct. 1972

3. "Assessing Potential Ocean Pollutants," Report to National Research Council, NAS, 1975

4. "The Environmental Quality Monitoring Report," OCS Task Team, NOAA, Feb. 1976

APPENDIX A.   PARAMETER REQUIREMENTS

GENERAL CHEMICAL PARAMETERS

- acidity
- alkalinity
- arsenic
- asbestos
- BOD
- boron
- calcium
- carbon, inorganic
  - carbon dioxide
  - carbonates
  - bicarbonates
  - carbon monoxide
- carbon, organic
  - dissolved particulate
  - total (TOC)
- chlorides
- chlorine
- chlorinity
- chemical oxygen demand (COD)
- cyanide
- dissolved oxygen
- dissolved silica (silicates)
- fluoride
- hardness
- hydroxides
- iodine
- metals
- (dissolved, particulate, total)
  - aluminum
  - antimony
  - barium
  - beryllium
- o cadmium
- o chromium
  - cobalt
- o copper
  - iron
- o lead
  - magnesium
  - manganes
- o mercury
  - molybdenum
- o nickel
  - potassium
  - selenium
  - silver
  - sodium
  - thorium
  - tin
  - titanium
  - vanadium
- o zinc
- nitrogen
  - ammonia
  - nitrate
  - nitrite
  - urea
  - amino acids
  - total
- orthophosphate
- phosphorus
  - phosphates
  - organic phosphate
  - total phosphate
- pH
- redox potential
- sulfur
  - sulfates
  - sulfride
  - sulfite
  - hydrogen sulfide

GENERAL PHYSICAL PARAMETERS

- bottom topography
- color
- conductivity
- current direction
- current speed
- density depth odor
- optical properties
  - transmission
  - scattering
  - ambient light
  - extinction
- salinity
- solids
  - dissolved
  - floating
  - settleable
  - suspended
  - total
- suspended particulates
  - particle shape
  - particle size distribution
  - total suspended load
- temperature
- wave direction
- wave height
- wave period
- turbidity
- sound speed
- light penetration
- upwelling & downwelling radiance
- visibility range
- sediment type and deposition
- cloud cover
- precipitation
- wind speed and direction
- subbottom topography

Radioactive Materials

- gross alpha
- gross beta
- gross gamma
- gamma spectroscopy
- Americium - 241, 243
- (N) Argon - 40
- Barium - 140
- Beryllium - 10
- (N) Calcium - 40
- (N) Carbon - 14
- Cerium - 141, 144
- o Cesium - 134, 137
- Cobalt - 158, 160
- Iodine - 131
- Iron - 55, 59
- Lead - 210
- Neptunium - 239, 236, 237
- o Plutonium - 239, 240
- Polonium - 210
- (N) Potassium - 40
- Protachtinium - 231
- Radium - 226, 228
- Radon - 222
- (N) Rubidium - 87
- Ruthenium - 103, 106
- Strontium - 89, 90
- (N) Thorium
- Tritiated Water
- (N) Uranium - 235, 238

BIOLOGICAL PARAMETERS

- algae
  - macroalgae
- bacteria
- benthic organisms
  - microbenthic organisms
- coliform
- epiflore
- epifauna
- fish demersal
  - pelegic
- invertebrates
- nerkton
- plankton
  - phytoplankton
  - zooplankton
  - ichyoplankton
  - periphyton
  - macrophyton
  - neuston
- viruses
- under ice biota
- birds
- mammals
- assimilation ratio
- biomass
- ATP
- BOD
- chlorophyll a
- chlorophyll b
- chlorophyll c
- heterotrophic uptake
- setting avility

Hydrocarbons

- total aliphatics
- total aromatics
- C_{10}, C_{11}, C_{12}
- C_{13}, C_{14}, C_{15}
- C_{16}, C_{17}, C_{18}
- C_{19}, C_{20}, C_{21}
- C_{22}, C_{23}, C_{24}
- C_{25}, C_{26}, C_{27}
- C_{28}, C_{29}, C_{30}
- C_{31}
- pristane
- phytane
- o-xylene
- 1-propyl benzene
- N-propyl benzene
- indan
- biphenyl
- dimethyl naphthalene
- trimethyl naphthalene
- fluorence
- phenanthrene
- anthracene
- 1-methyl phenanthrene
- fluoranthene
- pyrene
- benz (A) anthracene
- chrysene
- perylene
- dibenzothiophene
- benzo (A) pyrene
- benzo (E) pyrene

o higher priority   (N) naturally occuring

U.S. DEPARTMENT OF ENERGY

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The Department of Energy is certainly pleased to be able to participate in this meeting on water quality sensing because the DOE sees water quality as a major concern. Because we have not had a long time to prepare this talk, we have been unable to talk to the large number of people doing analytical work with the Department.

It seemed therefore appropriate to discuss a variety of projects done at Lawrence Berkeley Laboratory which are representative of types of water quality sensor research supported by the DOE. The types of research done in water quality can be broken down into three categories:

- Basic Research
- Application of Developed Techniques
- Analysis of Instruments, Systems and Strategies

Basic Research involves investigation and development of the most elemental parts of the technique including the detector and the electronics. It is possible that at this time the sensor may never touch water. Next the sensor is tested and proven in a laboratory situation. Research involving the application of developed techniques involves taking the sensors developed in basic research and applying them to the environmental situation. It is, of course, always necessary to continuously analyze the instrumentation systems and strategies being used and developed with respect to the water quality parameters which must be determined. One must consider the pollutants and parameters themselves, the regulatory standards and the recommended water quality criteria as a basis for evaluating the sensors available. Clearly one must also examine and evaluate the sensors themselves, and the scope and adequacy of the monitoring system and the strategy behind it. The information gleaned from this analysis should be readily available.

All three types of research are represented at LBL. The various projects are as follows:

1. Basic Research — Environmental Instrumentation and the Instrumentation and Environmental Research Groups
    - semiconductor detector development

		• XRF development • anodic stripping voltammetry
2.	Applied Research	OTEC Project (Ocean Thermal Energy Conversion) • artificial substances for in-situ growth • in-situ thermal gradient thermal conductivity • the Fish--in-situ water quality monitor
3.	Analysis	Environmental Instrumentation Survey

The Environmental Instrumentation Group has, over the last decade, made significant advances in the use of semiconductor detectors, particularly as applied to non-dispersive (energy dispersive) X-ray fluorescence (XRF) spectrometry.

They have built XRF spectrometers with high resolution by significantly improving the electronics. After developing an instrument which worked satisfactorily under laboratory conditions, they have automated and computerized it, and it has been working for one and a half years with only two minor breakdowns. Although the instrument is currently used to monitor air particulate composition, the adaptation of the instrument to samples from water systems, particularly suspended solids or sediments, would not be a problem.

Another instrument, working on a wavelength dispersion principle, has been developed to monitor sulfates. It is expected to operate in the field for up to 3 years.

The anodic stripping project, conducted by Clem et al., is exploring the means to enhance the sensitivity and broaden the applicability of the technique. Already Clem is able to detect lead in a 15-ml cell at 40 ppt (0.04 ppb); if the cell were flow-through type Clem could extend the sensitivity to less than 10 ppt. Although his instrument is usually used in the lab, Clem notes that it encounters no interference effects in the presence of sewage and saline waters. Clem is currently attempting to develop resin coated electrodes, which would extend the range of metals he is already able to measure.

The OTEC group has developed a variety of novel techniques for determining water quality parameters. The project involving artificial substances used for substrate in situ growth is an excellent technique for determining primary and secondary growth, ATP, and composition of algae. It has been used effectively on the Truckee River in California. The technique has two drawbacks: first, it requires substantial intelligent human effort and secondly, the monitors tend to annoy fishermen or interest little boys, and unless hidden carefully, seem to end up in the bushes. Vandalism of one form or another is an important problem to any on-site instrumentation. Blinkers used to mark mussel beds monitored in San Francisco Bay are now reputed to light many windows in Sausalito.

Most applicable with respect to this conference is "The Fish," a multipurpose probe which has been used to monitor depth temperatures,conductivity, pH, redox potential, sulfide ion activity and ambient light while being towed behind a boat. It has been used in a variety of marine and estuarine situations, but is not limited to salt waters. In order to install it for long periods of time it would be necessary to solve some calibration problems and to install a cassette or transmitter.

The Environmental Instrumentation Survey Group has for the last few years reviewed the instrumentation commercially available for monitoring a variety of pollutants in water and the principles behind their operation. We provide material concerning the pollutants and their forms and characteristics, their sources, the effects they have on the environment and human health and the methods used to control them. We also provide information regarding developing techniques, so that the reader can be aware of the state of the art even if it is not currently commercially available.

In conducting the survey, we have certainly noted the lack of sensors available for long term in situ monitoring. We also recognize that with the current regulations and with the important need to understand and protect our aqueous environment, it is essential to accurately and precisely monitor a wide variety of water quality parameters on a real time basis at a realistic cost. We have also noticed an unbalanced emphasis on performing quantitative analyses for the known or suspected pollutant instead of performing at least sporadically qualitative analyses for unsuspected pollutants. These unknowns can be detrimental themselves, but they also can have either a synergistic or antagonistic relationship to other pollutants with respect to measurements and environmental or health effects. One of the other drawbacks that was noticed in our analysis was that most environmental programs have ignored metallic speciation entirely. Yet, it is well known that organic mercury is far more toxic than is inorganic mercury, and the CR(VI) is potentially carcinogenic, whereas CR(III) is more harmless.

To summarize, the Department of Energy wishes to express its major concern for water quality. Its interests are not limited to one geographical area, but are nation- and world-wide, as is demonstrated by the satellite program which has been mentioned earlier in these discussions. Research is being performed on most categories of water--inland waters--lakes and rivers, surface and groundwater; in enclosed bays and estuaries and in the ocean. The quality of water examined ranges from fresh mountain streams to estuaries, to polluted rivers and sewage. The parameters examined are as diverse as the water monitored. Research is not limited to one area, but encompasses the range from basic research to analysis of strategies.

The DOE clearly sees water quality as a major concern and hopes to be able to help solve the problems which are being considered by this workshop.

U.S. ARMY CORPS OF ENGINEERS

by Earl E. Eiker
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The civil works program of the Corps of Engineers involves the entire spectrum of water resources development and management. The Corps' role traditionally has involved planning, design, construction, operation and maintenance of water resources projects to meet numerous purposes. These purposes include flood protection, navigation, water supply, fish and wildlife enhancement, hydropower, water quality control and recreation. The national concern for the preservation and protection of the environment has resulted in legislation that makes environmental quality an additional consideration in water resources development. In order to address this concern, water quality data collection programs are maintained at most Corps projects. Data generated are used primarily in connection with project operation and environmental impact analyses. The man hours required to conduct the data acquisition and analysis for these programs is great. An attractive alternative to manual collection of data is greater utilization of in situ monitoring systems that can rapidly, accurately and cost effectively accomplish this task.

Presently, all Corps field offices as well as research labs are using water quality sensors to measure water quality parameters in the field. The distribution of these offices is throughout the entire United States. Because of this wide geographical distribution, there is a corresponding wide range of environmental conditions associated with these sensor applications. Sensors have been used in marine, estuarine, river, stream and lake environments in areas subject to large changes in temperature, wind, precipitation and many other climatological and hydrological conditions. In addition, the remoteness of several locations has created additional problems relative to servicing and maintenance.

The diversity of the Corps' water quality data collection effort makes for a wide-range of parameters of interest. To date, sensor applications have been limited by the availability of equipment. Also, the intended use of the data has a large bearing on sensitivity requirements. Some parameters of interest and limits of accuracy (where appropriate) required are: 1) temperature (0.1° C), 2) dissolved oxygen (0.5 ppm), 3) optical properties - light transmission and scattering, 4) total and ortho phosphate (0.1 ppm), 5) ammonia nitrogen (0.1 ppm), 6) nitrate nitrogen (0.1 ppm), 7) organic carbon (1 ppm), 8) pH (0.2 units), 9) eH, 10) specific conductance (5 mhos), 11) oxygen reduction potential, 12) specific ion measurements (particularly chloride and sulfide) and 13) total dissolved gases (percent saturation). Along with sensitivity requirements, it should be noted that specification of accuracy, instrument response time and stability are also very important sensor criteria. Often a sensor can be very sensitive to change in parameter concentration but inaccurate at the same time.

Presently, sensor deficiencies are related primarily to lack of reliability over extended periods of time. This fact greatly limits the application of available sensors. These problems are caused by exposure to sunlight, algae growth, accumulation of sedimentation and other debris, temperature variations, salinity and ice cover. Also, sensors are, for the most part, fragile and thus easily damaged during shipment and use. Calibration of sensors under field conditions remains a serious problem.

Two research laboratories within the Corps have done a limited amount of developmental work with water quality sensors. The Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire, is presently conducting a study on the use of an airborne spectoradiometer to measure turbidity in water bodies as well as studies to measure and monitor soil moisture under field conditions. The Waterways Experiment Station at Vicksburg, Mississippi, has recently completed a comparative study of several commercially available sensor packages to determine suitability for field application. Several Corps field offices are also engaged in a variety of applications efforts.

Future sensor requirements are very difficult to predict. There is a definite need to improve those sensors which are presently available in order to increase reliability and this should be the first priority. Work is also needed in the area of standardization of signal output from sensor packages. The growth of interest in sensors over the last several years should provide the impetus needed for development of improved instrumentation.

All Federal agencies having a responsibility in the water quality area have an interest in water quality sensor development. Many of these agencies have on-going programs in sensor development and/or application. However, very little opportunity now exists for coordination of activities and sharing of experiences. This workshop is a good beginning but unless some form of formal coordination is established among the various agencies, the momentum may be lost.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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From its earliest days, the space program has been concerned with the problems of water quality measurement and control. In 1971, the NAS-NRC Committee on Toxicology appointed a Panel on Water Quality in Manned Spacecraft. Its charter included the performance of studies and the submission of recommendations on both potable and nonpotable water contamination problems.

Several studies were undertaken to investigate integrated water and waste management systems for future spacecraft. One such study, performed by the General Electric Company, led to the development of a prototype system that served a multitude of functions ranging from waste collection and disposal to water reclamation and purification.

The potable water supply system developed for Skylab missions incorporated an inflight iodine bactericide monitoring and control unit. This compact subsystem consisted of a water/iodine concentration sampler, color comparator, reagent container assembly, waste sample container and iodine injector.

There are numerous other situations within the NASA program that have called for unique technological approaches designed to deal with the special water quality control problem encountered in the closed environment of a spacecraft.

But there is another side to the NASA interest. Embodied in the words of the legislation that created NASA in 1958, is a mandate that binds us to "the establishment of long range studies of the potential benefits to be gained from the utilization of aeronautical and space activities for peaceful and scientific purposes." In addition, we are required to apply these technologies "to the conduct of peaceful activities within and outside the atmosphere."

It is this aspect of the NASA program that is of interest today. It is this aspect that has brought us here from NASA Ames in California, from Langley in Virginia, Lewis in Cleveland, Ohio, and from Headquarters.

The work we will be discussing with you during the week comes under the auspices of our Office of Space and Terrestrial Applications.

As we are all aware, the environment for Federally supported R&D has changed markedly over the past few years. Public scrutiny has increased, and we are being asked at an ever increasing frequency to justify the commitment of public resources to research that is often characterized by laymen as esoteric, and unrelated to the real needs of society. As with other R&D organizations, NASA has had to face more stringent reviews of its R&D budget. We have accepted the challenge and, since the launching of the last Apollo flight, have strived to develop a strong program directed towards applying space and space technology to the problems and needs of mankind. Also, each year a certain amount of these resources is used on programs aimed at utilizing NASA's competence as well as its technology in dealing with needs that are not directly related to the aerospace arena.

We lump these latter activities into a single classification. We call them Technology Transfer projects. Last year, we allocated approximately 15 to 20 million dollars to such projects. More than 5 million of this amount was used in providing information about NASA's technology to prospective and active users of this technology. The balance was used on projects to implement, modify, and develop technology to meet specific user needs.

I would suspect that many of you, or certainly the agencies you represent, have been involved at one time or another with this NASA program.

In Situ Water Quality Sensors

I have tried to present, in capsulized form, the raison d'etre for NASA's involvement in the field of in situ water quality measurement. It represents one aspect of a broad program in which NASA, with the help of outside users, has determined that the agency's technical competence can be used to the advantage of the non-aerospace community.

I shall return to the subject of technology transfer later in my talk. But right now, we need to deal with the topic at hand. What are NASA projects in the area of in-situ water quality sensor development?

I should begin by describing some activities undertaken as part of a long-standing joint NASA/EPA Interagency Agreement. Since 1972 a cooperative program has existed between the EPA Office of Research and Development and NASA. Under this Agreement, we have been evaluating remote sensing techniques such as four-color laser systems, multi-spectral scanners, multispectral photography, dual differential radiometer, microwave radiometers, thermal imagers, and infrafed photography for water quality monitoring. As a necessary part of this program, numerous field operations which required water sampling and in-situ water quality measurements have been carried out--primarily along the East coast in coastal and estuarine waters. Usually in situ measurement capabilities of other agencies (EPA, Corps of Engineers, NOAA, and various university groups) are depended upon in the coordinated field test program requiring complementary remote and ground truth measurements of water quality. In general, commercially available sensors are used for the limited in situ data obtained. Most of the measurements of interest still require water samples to be taken back to the laboratory for anlaysis. For example, on a recent water quality field experiment in the James River near Hopewell, Virginia, of the 25 parameters of interest, only two were measured in situ. These were temperature and secci depth. Of the other 23 only 5 were considered measurable with commercial in situ sensors. Difficiencies of in situ sensors include high maintenance, inadequate sensitivities, unproven or unaccepted standards, high operator skill requirements, short lifetime, and, sometimes, cost.

Responding to needs cited by EPA Region V, the EPA Monitoring Operations Division, Las Vegas, Nevada, requested NASA assistance in devising and implementing small portable water quality monitoring systems for use by all EPA regions. This request occurred in 1976.

For their needs, the EPA envisioned modular design concepts, with growth potential, utilizing NASA systems integration technology along with potentially low-cost microelectronics for use in on-board processing and data transmission components and techniques. NASA is interested in this project because of its potential benefit in providing low-cost automated in situ ground truth stations for calibration and validation of remotely-sensed environmental data. Under the resulting interagency agreement, NASA will demonstrate a one-person deployable water quality monitoring system. The package will accept and store data from a large variety of in situ sensors and can take water samples for later laboratory analysis. The data will be stored in a nonvolatile electronic memory system utilizing NASA technology. The system can be deployed and retrieved from a small Bell 47 helicopter (2 or 3 place) or from a small boat.

Also, under the same agreement, a small, helicopter-borne water-quality monitoring probe is being developed by using a combination of basic in situ water quality sensors and physical sample collector technology. The probe is a lightweight system which can be carried and operated by one person as a passenger in a small helicopter typically available by rental at commercial airports. Real-time measurements are made by suspending the water quality monitoring package with a cable from the hovering helicopter. Designed primarily for use in rapidly assessing hazardous material spills in inland and coastal zone water bodies, the system can survey as many as 20 data stations that are up to 1.5 kilometers apart and it can accomplish this in 1 hour. The system provides several channels of sensor data and allows for the addition of future sensors. It will also collect samples from selected sites with sample collection on command.

An EPA Spill Response Team member can easily transport, deploy, and operate the water quality monitoring package to determine the distribution, movement, and concentration of the spilled material in the water body. Test flights with the helicopter-borne water-quality monitoring system have shown that it has great promise for rapidly monitoring hazardous material spills, and collecting other data.

Another project that has received support from EPA--including this Laboratory--involves the application of an electrochemical detection method to the monitoring of fecal coliform concentrations in water.

For the past 3 years, research has been underway at the Langley Research Center to develop an automated in situ coliform monitoring system. The electrochemical sensor used to detect coliforms was developed by Wilkins and Stoner. The technique was based on measuring the time of hydrogen evolution as a function of inoculum size. A linear relationship was established for this parameter. A prototype system for monitoring levels of fecal coliforms was evaluated in both fresh water and estuarine water. These evaluations were performed in conjunction with EPA Region II. Thirty-two samples were processed by the in situ electrochemical system during the evaluation. Correlation with laboratory standard methods for determining fecal coliforms was good for 14 samples, fair for 8 samples, poor for 6 samples, and undetermined for 4 samples due to faulty electrodes and insufficient laboratory data. As a note of explanation for these qualitative judgements, 'good' indicated that the laboratory data were within the range of the predicted values, 'fair' results had differences by a factor of 10 to 100, and 'poor' results had differences greater than 1000.

Very early in the development of the in situ monitoring system, an interagency agreement was developed between EPA (Region II) and NASA. Four tasks were delineated. One of these tasks detailed the conditions for a cooperative field evaluation of the in situ system at Caven Point, New Jersey. This agreement proved to be an excellent arrangement between the systems development agency, NASA, and the user agency, EPA. It provided NASA with the users requirements and at the same time afforded EPA the opportunity to become familiar with the system.

In another project, we have been developing a system that utliizes NASA's experience in data acquisition and processing techniques as applied to continuous, near real-time water quality monitoring and control. It has been directed towards demonstrating the feasibility of the concept of continuous, on line monitoring.

In 1971, NASA began a special study applying the technical approaches and design philosophies of closed systems to the utility system of a 500-dwelling-unit garden apartment complex. These studies led to an interagency agreement between NASA and HUD (Department of Housing and Urban Development) relating to the design and development of a MIUS (Modular Integrated Utility System). Basic functions to be supplied by the MIUS included integration of electrical power generation, water processing, solid and liquid waste management, and environmental conditions, and also the use of residual energy for utility functions. Only production hardware items were to be incorporated in designs and no building system changes were to be made. NASA's support of this integration and test program resulted in a project to develop an automated water quality monitoring and control system to insure the safety and quality of treated wastewater so as to permit its reuse (for non-potable purposes) in systems such as the MIUS.

Our studies of water supply planning and wastewater reclamation activities indicated a growing concern was motivating responsible local, state, and national organizations to give serious consideration to reuse applications. California, for example, has begun numerous reclamation and reuse projects. The most notable of these projects was the reuse of effluent from the Lake Tahoe Tertiary Treatment Facility for recreational application in the Indian Creek Reservoir. A study performed for NASA further noted that many authorities in the water/wastewater management field were convinced that the long-term solution to the problem of insufficient water resources was in wastewater reclamation and reuse. The City of Denver, Colorado, for example, has been engaged in the planning for facilities that will reclaim 100 mgd/day by 1986 for addition to the public water supply. The City of Denver hopes to supply 2 percent of its total water needs through the reuse by the year 2000. On the basis of these studies, there appeared little doubt that wastewater recycling and reuse in the domestic and civil sector would become common practice in the United States and the world in future years.

These study results, together with other NASA commitments, resulted in a project to develop an automated water monitoring system by applying space developed sensors and technology. The basic concept should be applicable to all facets of water monitoring--from natural water bodies to municipal drinking water supplies to industrial and municipal wastewater.

The basic system has been installed by NASA in a converted surplus radar van. Preliminary checkout was accomplished at the City of Houston's southwest wastewater plant. The on-going field test of the system is a joint demonstration test with Santa Clara Valley Water District (SCVWD) at their experimental wastewater facility. This facility was built with funding help from EPA and the State of California. It is located on the Palo Alto wastewater treatment facility grounds. This field demonstration test will evaluate the feasibility of the concept as a practical means of monitoring water quality and thereby measure the effectiveness of the wastewater treatment by this plant.

Although simple in principle, the actual system is complex in fact. I must, therefore, defer its detailed description to the Workshop sessions. Suffice to say, the system uses 18 commercially available sensors to analyze 14 parameters. In addition, the system incorporates some NASA developed sensors to monitor bacteria and trace organics. In addition, we are exploring some other unique approaches to monitoring biomass and viral contamination in water. These are not wet chemistry approaches but rather are designed to rapidly provide an electronic signal that measures concentration. This signal can then be readily digitized for storage and processing.

Other instruments developed within the NASA program for water quality determination are included in the Appendices to this narrative. Finally, I will make mention of some fascinating research that we have been supporting, under a university grant, that is aimed at developing miniature, self-contained, highly reliable in situ water quality sensors. This work, performed under the auspices of Professor C.C. Liu of the University of Pittsburgh, is based upon small scale-electrochemical and immobilized enzyme concepts. To date, successful development of a phenol sensor as well as miniature pO_2 and pH sensors has been accomplished. Dr. Liu's work is now being directed towards the application of enzymatic reactions to the monitoring of trace metal ions in water. This work originated as part of a NASA program to develop an in situ water monitoring system for use by EPA Region V for their oversight of the Great Lakes Basin. This research has continued, although the proposed joint program was aborted.

Conclusion

This then briefly summarizes the NASA activities that we will be discussing with you through the course of this week. I suspect they may not be the only projects in water monitoring being undertaken within the agency. One of the principal activities for the coming year will be to try to coordinate and integrate NASA's programs in water quality assessment. That, in fact, is one of the main reasons for our rather heavy attendance at this Workshop.

I hope you recognized that laced through all our projects in this area is the close interrelationship with some identified users of the technology. I am again returning to the importance of the transfer aspects of our program. Our objective here is to develop applications of space technology and the capabilities of

NASA's R&D organization to non-aerospace problems. In the coming years we hope to strengthen our efforts in this area. But the true measure of our success depends upon the cooperation and support that our endeavors receive from you, the eventual implementers and users of this advanced technology.

NASA has no chartered responsibilities in water resources management but we have a deep and abiding desire to apply what we have learned in our aerospace missions and what we have built--an R&D institution designed to accomplish difficult technological objectives of this important national concern.

In addition to these summary remarks for verbal presentation at the Workshop, the following Appendices are attached for inclusion in the Workshop report to provide additional detail on NASA water quality sensor development activities:

Appendix A - Automated Water Monitoring System

Appendix B - Electrochemical Method to Detect Coliform Bacteria

Appendix C - Miniaturized Electrochemical and Immobilized Enzyme Sensors for In-Situ Water Quality Measurement

Appendix D - Other Activities within NASA
- The Instrumental Detection of Viruses
- A Neutron Gamma Ray Detection and Monitoring System
- A Thermal Plume Monitoring System
- Acoustic Tracking of Woodhead Sea Bed Drifters
- A Portable X-Ray Fluorescence Spectrometer
- An Implantable Acoustic-Beacon Automatic Fish Tracking System

APPENDIX A. AUTOMATED WATER MONITORING SYSTEM

This project has been conceived to demonstrate the feasibility of real-time or near real-time automated analysis of overall water quality by applying space-developed sensors and technology. The basic concept should be applicable to all facets of water monitoring from reservoirs to municipal drinking water supplies to industrial and municipal wastewater treated effluents.

The basic laboratory has been installed by NASA in a converted surplus radar van. Preliminary checkout of the basic laborabory was accomplished at the City of Houston's Southwest wastewater plant. The on-going field test of the laboratory is a joint demonstration test with Santa Clara Valley Water District (SCVWD) at their experimental wastewater facility build with funding help from EPA and the State of California. It is located on the Palo Alto wastewater treatment facility grounds. This field demonstration test will evaluate the feasibility of the concept as a practical means of monitoring water quality and thus the effectiveness of the wastewater treatment by this plant.

As stated above, the SCVWD plant is an experimental plant and thus equipped with several different waste treatment processes including lime settling, filtering, activated carbon treatment and ozonation. Furthermore, the influent to this plant is the effluent from the City of Palo Alto wastewater treatment facility (basic sludge plant), and the primary purpose of the experimental plant is to evaluate the different wastewater treatment methods to determine their effectiveness in producing water that can be reused (recycled water).

Santa Clara Valley Water District (SCVWD) plans to use half the plant output of four million gallons a day for injection into the underground aquifers of the lower San Francisco Bay to see if the intrusion of the saline water from the Bay into these aquifers can be slowed, stopped, and eventually reversed. The other half of the plant output will be sold for use as irrigation water. First customers will be the City of Palo Alto and Mountain View for irrigating a golf course and Baylands Park, respectively. There is a good possibility that both NASA and the Navy may also be using this water for irrigation and washing aircraft in the near future. Thus, knowing the quality of the wastewater in real time is important, and documentation becomes imperative for future reference.

Figure A-1 shows the flow through the SCVWD experimental plant schematically and also shows the locations in the wastewater processing where continuous samples are drawn into the WMS trailer for automated water quality analysis. Figure A-2 shows schematically how the water samples are conditioned and distributed to the sensors on the WMS trailer.

The laboratory developed by NASA uses 18 commercially available sensors to analyze 14 parameters to support the NASA-developed biological and trace organic sensors. These commercial sensors have been reworked for automated operation and measure such parameters as: total oxygen demand, total organic carbon, pH, turbidity and temperature. The bacterial sensors developed by NASA are also automated and are capable of reducing the analysis time required from days to hours; they include a sensor for fecal coliform total bacteria, and total living bacteria. A trace organic sensor using twin gas chromatograph columns has been adopted from an instrument specifically developed for NASA's Viking Project. This instrument will be used to detect suspected carcinogenic contaminants in water. These sensors are expected to provide SCVWD with data which will help them evaluate operational efficiency of their plant. All activities of the trailer, from sampling to sensor calibration and report generation, are computer controlled.

Twin NOVA 1200 mini-computers are used for the above activities. (Figure A-3).

On the following pages, the sensors are described followed by summaries of operational problems that we have encountered to date and finally some typical daily results are shown.

SENSORS

The sensors are grouped into the general categories, commercial and NASA. The group of commercial sensors is described first.

COMMERCIAL SENSORS

This group of sensors was obtained from government surplus property or bought off-the-shelf from a commercial supplier. In each case the sensors and their support hardware and electronics were reworked to make them compatible for automated operation. As stated above some of the sensors and packaging were obtained from surplus property and were not the optimum or latest state-of-the-art sensors for the application. Consequently, as with the total nitrogen sensor, problems have been encountered with reliability and we have decided to replace them as they fail.

Total Organic Carbon (TOC)/Total Oxygen Demand (TOD)

The Astro Ecology Corporation analyzer simultaneously determines TOD and either total carbon or TOC on aqueous samples containing solid particulates up to 2000 micrometers in diameter. Dual measurement ranges of 0-10 ppm or 0-500 ppm of carbon and 0-1000 ppm of TOD are available.

Fifty ml/minute of sample is continuously pumped into a mixing chamber and gas-scrubber assembly where it is mixed with hydrochloric acid to reduce the pH to 3. A portion of the scrubbed, carbonate-free sample (4 ml/min.) is pumped into a combustion chamber and combined with a metered air stream (79% oxygen). The air provides the oxygen for combustion. The sample remains in the chamber at 850°C long enough for full combustion to occur. The products of combustion and excess air leave the reactor and enter a water-cooled liquid/gas separation assembly which removes condensable vapors. The remaining gases are routed to an infrared analyzer where the amount of carbon dioxide is measured and converted to units of TOC.

THE TOD analyzer determines oxygen demand for hydrogen, nitrogen, sulfur, and carbon compounds found in the sample water. It receives the noncondensable gases from the TOC analyzer following the carbon dioxide analysis and passes them through a solid electrolyte oxygen detector. The oxygen depletion, based on the amount of air fed to the reactor, is measured and translated into units of TOD.

Total Nitrogen (TN)*

The IBC/Berkeley Nitrogen Analyzer receives the non-condensable combustion gases from the TOD analyzer and determines the concentration of nitric oxide, by measurement of the potential between two electrodes. During the combustion at 850°C, all nitrogen in the sample has been converted to nitric oxide, thus a total nitrogen reading is provided by the instrument in the range of 10 to 10,000 ppm nitrogen.

Hardness

An Orion Model 1132 Hardness Analyzer continuously monitors the sample stream for hardness, a measure of calcium and magnesium ions in water. The technique used is proprietary to Orion Instrument Company. However, in general terms, it involves the chelation of all devalent ions by a complexing agent, followed by the addition of a "substitution" ion which selectively releases calcium ions. A "tag" ion is added at molar concentrations 100 times greater than the maximum possible ionic strength. A reference electrode is selective to this tag ion, and the sensing electrode is selective to the substitution ion. The electrodes are connected to the analyzer's electronics system, which gives a direct hardness reading on a 4-cycle logarithmic scale calibrated to read from 0.1 to 1000 mg/l.

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*Note: This unit has been worn out and several models of nitrogen analyzers are currently being evaluated as a replacement.

Nitrate

A Delta Scientific Model 8138-153105-002XX1 Nitrate Analyzer continuously measures nitrate/nitrite concentrations in the sample stream by spectrophotometric analysis. Nitrates are reduced to nitrites in a cadmium reducing column. The nitrates are then reacted with sulfanilamide and N-1 Napathy-Ethylendiamine Hydrochloride (NEDA) in an acid solution to form the azo dye. The color intensity developed is a measure of the nitrate plus nitrite concentration in the sample. The concentration of nitrites may be determined separately by bypassing the cadmium column. Nitrate/nitrite concentrations above 0.4 ppm are too dark for useful discrimination. Therefore, dilution of the sample is required for most measurements.

pH

The Great Lakes Instruments (GLI) Model 70 Analyzer measures pH for inprocess and pollution applications. The GLI probe uses their Differential Electrode Technique to compare a pH electrode to a standard electrode containing a chemical pH standard. The probe is housed in a PVC tee (as described for the chloride ion probe) to increase the flow velocity by the probe. An Orion Model 401 specific ion meter provides a direct readout of pH using an Orion 91-01 pH electrode and a Beckman 19033 Lazaran process electrode. The pH electrode has a range of 2 to 11 pH units. Both electrodes are mounted in a small tank that provides continuous monitoring capability.

Total Residual Chlorine

An Orion Model 1125 Chlorine analyzer measures the residual chlorine in continuous samples by the potentiometric method. It operates on the principle that chlorine will liberate free iodine from potassium iodide solutions when the pH is 8 or lower. The sample is mixed with a reagent and pumped through a reaction heater and constant temperature analysis chamber. In the chamber, the mixture passes between a sodium electrode and a redox electrode. The electrodes are connected to the analyzer's electronics system which gives a direct chlorine concentration reading on a 4-cycle logarithmic scale calibrated to read from 0.1 to 1000 mg/l.

Sodium

The Beckman 194204 Model 9415 Sodium Ion Analyzer determines the concentration of sodium in a sample stream by measuring the potential between a Beckman 633951 Sodium Ion Electrode and a Beckman 19604 reference electrode. The electrode potential is directly proportional to the logarithm of the active sodium concentration. The response of the sodium electrode can be affected by several other monovalent cations. Usually, hydrogen is the only interfering ion encountered. To eliminate this interference, all solutions are pH adjusted with ammonia to suppress the hydrogen ion concentration. Temperature control is provided by a heat exchanger located upstream of the electrode flow chamber.

Temperature

Two Action Pac Resistance Thermal Detectors (RTD) are used to measure sample temperatures. The RTD probe detects changes in potential between two electrodes as the temperature changes and converts this to a 0 to 5 volt signal. The probe is sensitive to 0.1°F and reads from 0 to 200°F.

Turbidity

A Sigrist Photometer Turbidimeter Model UP 52-TJ determines the turbidity of a continuous sample stream by comparison with a nephalometric standard. The Model UP 52-TJ has four measuring attachments of different ranges. Two of the units use falling-stream flow cells with ranges of 2 to 1000 and 2000 to 15,000 Jackson Turbidity Units (JTU); one uses a surface scatter-flow cell with a range of 5 to 100 JTU, and one uses a splash-flow cell with a range of 0.5 to 20 JTU. All of them use a dual beam optical measure bridge. In the DAS, the units of measurement are converted to mg/l SiO_2.

The Honeywell Model 551201-02-01 Turbidity sensor has an optical head and a sampling tank for on-line analysis. A beam of light is focused by a lens system down into a falling sample. A photocell detects the light reflected by particles in suspension and supplies a proportional millivoltage to the signal conditioner. The sensor has a nominal range of 0 to 25 Formazin turbidity Units (FTU).

Ammonia

A Delta Scientific Model 8119 Ammonia Analyzer continuously measures ammonia in sample water by spectrophotometric analysis. The intensity of the blue color developed by the reaction of ammonia with phenol and hypochlorite in alkaline medium is proportional to the concentration of ammonia in the sample. The analyzer has a minimum sensitivity of 0 to 1 ppm ammonia, and no upper limit.

Chloride

A Great Lakes Instrument (GLI) Chloride Ion Probe measures chloride by GLI's patented Differential Electrode Technique. The GLI approach compares an Orion Model 94-17 solid-state chloride electrode to a standard electrode containing a chemical chloride ion standard. The probe is housed in a 1 1/2-inch PVC tee that has been modified to reduce interior volume and provide a rapid flow past the probe. Before reaching the probe, the sample is mixed 50:1 with an ionic strength/pH adjuster. The probe has a sensitivity range of 10^0 to 5×10^5 moles per liter of chloride ion. It is relatively free from interferences except for sulphur, bromide, iodide, and cyanide.

Conductivity

The sensor used to measure the ionic content of the water sample is a Beckman Type R15 Solu Bridge Conductivity Indicator with a temperature-compensated epoxy flow-through cell, type CEL-VDJ4-KF. The cell constant is 4.0 permitting measurements in the range of 0 to 2000 umhos/cm.

Dissolved Oxygen (DO)

A Delta Scientific Series 8310 Automatic Analyzer continuously measures dissolved oxygen in a sample stream with a tank-mounted DO probe. The patented probe consists of gold and silver electrodes mounted in a PVC body. A teflon membrane forms an oxygen-permeable barrier between the water being tested and the electrolyte in the probe. A voltage applied across the electrode and as oxygen passes proportional to its concentration. DO readings in mg/l and ppm in the ranges of 0 to 2, 0 to 10, or 1 to 20 are displayed.

The Honeywell Model 551011-00-01 dissolved oxygen sensor is a polarographic transducer consisting of a gold-silver-platinum alloy cathode and a silver/silver chloride anode immersed in an electrolyte cell. Its operation is similar to that of the Delta Scientific instrument.

NASA DEVELOPED SENSORS

The following four sensors were developed for water quality monitoring based on concepts developed by NASA in its space program.

Biosensor, Luminol-Carbon Monoxide

This sensor was developed for continuous real-time detection of total viable and non-viable biomass in water. The sensor employs the chemiluminescent luminol-hydrogen peroxide reaction with bacterial iron porphyrins and the carbon monoxide method to differentiate live from dead bacteria. Bacterial measurements in water samples using this sensor are accomplished within an hour. Essential hardware for this sensor consists of a photometer for measuring chemiluminescence, a peristaltic pump for proportioning sample and reagents and valves for sample selection and carbon monoxide treatment.

The sensor interfaces with the WMS deionized water system, 100 psig air, 28 VDC power, 120 VAC power, wastewater drain lines, CO gas line and the computer system. The sensor interfaces with the computer system for automatic control of the sensor operation schedule, continuous measurements of photometric cell output voltage, calculation of organism measured, and storage and retrieval of sensor results.

Coliform Sensor

The coliform sensor detects presence of total and/or fecal coliform organisms. It operates according to a "batch" process schedule with up to eight incubator cells in operation. The "batch" operation includes a four-phase operation: a) incubator cell cleanup, b) nutrient fill, c) inoculation and d) total and/or fecal coliform organism growth. The sensor interfaces with the WMS facility for deionized water, 100 psig air, 28 VDC, 120 VAC power, wastewater drain lines. The computer system provides automatic control of the sensor process schedule, monitoring and measuring individual incubator cell performance. In addition, it calculates total and/or fecal coliform organisms present in inoculum for each incubator cell and provides storage and printout of sensor results.

A second coliform sensor using the concept of electrical impedance changes in the selective incubation nutrient solution resulting from growth of fecal coliform bacteria has been developed. It is in final checkout along with parallel efforts to shorten the detection time via the use of optimum frequency.

Trace Organic-Gas Chromatograph

An existing gas chromatographic method has been adapted for the rapid in situ analysis of chlorinated organic compounds at the part-per-billion (1 ug per liter) level in water. This method uses two gas chromatographs (GC) connected in series through a system of valves and traps. The system operates automatically and small samples of water (120 microliters) are injected directly for analysis. The sample is injected through a sample valve into a preparative GC for separation of organic compounds from water. The organics are collected on a Tenax GC trap which is heated to transfer the organics to the analytical GC. In the analytical GC the mixture of trace organic compounds is separated and detected by an electron capture detector. The system is also equipped with a flame ionization detector for monitoring aromatic compounds such as benzene and chlorobenzene.

Viral Detector

This unit is in the development phase and various components are being built for assembly into a prototype instrument. The instrument is based on dyeing the virus and exciting the fluorescence of the dye-viral complex with a Laser beam.

Initial work showed ethidium bromide, a high quantum yield fluorescent dye combines with various types of enteric (polio and influenza) and bacterial viruses. The fluorescent signals of the dye-virus complex are enhanced 20 to 50 fold. The number of dye molecules bound and the fluorescence emitted per virus was found to be dependent on the number of base-paired regions of the viral nucleic acid. Viruses possessing either a doubled stranded DNA or RNA usually incorporated more dye molecules than single stranded viruses. However, even small single stranded viruses like polio or MS2 were found to incorporate enough dye molecules (400 virions) to be experimentally detectable with current photodetection technology provided the background noise is kept to a minimum. The fluorescent dye was found to be freely permeable through the protein coat of most viruses and where permeability problems existed, heating the virus for 30 seconds in buffered solution at 70°C was sufficient to overcome this barrier.

An argon excited flow microfluorometer with a digital readout component for rapid determination of viral titer in solution is under construction at the Block Engineering firm in Boston, Massachusetts. The instrument is designed to detect individual viral particles in a flow system containing less than 10 viruses/ml in a 10-minute observation time providing the background noise is eliminated or kept to a minimum. The laboratory instrument in its present state (without removal of background signals) has measured T2 virus at a concentration of 10^5/ml in a 10-minute counting time but its ultimate capability still has not been determined. Interference by background noise is still a problem but hopefully can be solved soon. The instrument is scheduled for delivery, assembly and testing in Ames in February 1978. Further experimentation will be required to optimize the instrument before it is integrated to a viral concentrator and eventually assembled as a unit for automated real time flow systems.

RESULTS

All sensor data for the entire month are stored on disc and at the end of the month, the data are transferred to magnetic tape. At this time or any time during the month, the data can be retrieved and displayed on the video screen or as tabular printout (Table A-1) or in graphical form (Figure A-4).

Currently the monthly data are reported in graphical form as daily averages. They are generated from the hourly averages stored on disc for each sensor and for each sample source. The hourly averages are summed and scanned to evaluate the daily average within one standard deviation (dashed line). The lower grid is used to report the hourly peak (dot-dash line) and the time of day the hourly peak occurred (numerals). These data are "validated" data, i.e., bad data have been purged from the hourly average prior to plotting. No other attempt has been made to alter the recorded results.

Table A-1 shows typical daily results for all the sensors onboard the WMS trailer with the exception of temperature, total oxygen demand, total nitrogen, sodium, chloride ion, dissolved oxygen, hardness and nitrate. These sensors were not operated on the 4 days used in this example. Only the TOD sensor, due to overheating of its electronics, and the worn out total nitrogen sensor were nonoperational. The results show that significant reductions in the monitored parameters do occur in the treatment process. For example, biomass reductions were on the order of 95 percent; turbidity reduction was about 28 percent and chloro-organics about 87 percent. The data indicate only nominal reductions in non-volatile organics (TOC) and ammonia during this period because the ammonia stripping and carbon absorber treatment processes in the plant were not activated. These results indicate how the data from the automated water quality monitoring system can be used to monitor the operational effectiveness of water treatment processes in a wastewater plant.

Figure A-4 shows the graphical monthly data format for dissolved oxygen. This is for the SCVWD reclamation facility "B" effluent water sample station 6 (see Figure A-1). Similar dissolved oxygen plots for any of the other five sample stations are also available along with similar plots for all other sensors.

The plots in the upper graph show the daily average reading (solid line) bounded by plus or minus one standard deviation (broken lines). The dispersal of the one standard deviation lines gives an indication of the fluctuation in the sample through the day. The lower graph shows the maximum hourly average peak for each day and provides a measure of how extreme the day to day maximum sample values were and, when compared to the daily average value, indicates the possible extreme variation in the water quality for that day.

SENSOR SHORTCOMINGS AND TYPICAL PROBLEM AREAS

Two modes of failure interrupt the continuous operation of the system. The first most common failure is computer malfunction due to either overheating (corrected by installing a blower in the chassis) or from running out of storage space. Installation of a larger computer would solve the latter problem. The second type of failure involves the sensor electronics. These failures occur primarily because the system is a prototype and many continuing changes are made. Also, surplus equipment was heavily used to minimize overall cost. These failures have not been serious and certainly are not expected with an operational system.

COMMERCIAL SENSORS

Probably the greatest problem has been that the commercial sensors used, or their associated electronics and hardware, were not engineered for continuous, automated, unattended operation and, thus, the reliability of the overall sensor packages tends to be poor for this application. The installation on the WMS trailer has experienced difficulties such as drift in the zero baseline of the TOD analyzer due to the sensor manufacturer placing the electronics in a high temperature environment, drifting of the chloride sensor and failure of the total nitrogen sensor. Other problems that have been encountered are contamination of the sensing elements and clogging in the feed lines to the sensors, gasket and pump impeller failures. Seal failures have been fairly frequent occurrences.

NASA DEVELOPED SENSORS

Biosensor, Luminol-Carbon Monoxide

This sensor is a first prototype and as such has operated very well. There are certain limitations, however. In particular, the system measures total living biomass and does not distinguish between dividing and non-dividing cells. Thus, the results do not correlate with standard plate counts. Also, in order to avoid clogging in the sample tubes (0.4 mm diameter), selective filtration is used which results in those clumps of bacteria, larger than the filter size, being removed from the sample. This lowers the sample bacteria level. A survey of the literature shows no acceptable methods are known for breaking up the clumps without affecting the actual bacterial colony. Some problems with retained contamination, when too weak a cleansing reagent is used or solution is used, remain to be solved. These are important but not necessarily debilitating problems.

Coliform

This sensor for the present is not completely automated; that is, the sample for the sensor is not automatically drawn from the overall sample stream. Contamination problems resulting from residual material in the sample feed line have been experienced. This hinders the automatic sampling procedure. Improvements in this area and in general cell sterilization procedures are being investigated. Some procedures which will help improve this sensor performance include (1) the variation of the sample replicates via better sampling and sample preparation techniques, (2) neutralization of anticipated sample interferring agents found in different water samples and (3) increased sensitivity and reduced detection time for the sensor.

Trace Organics

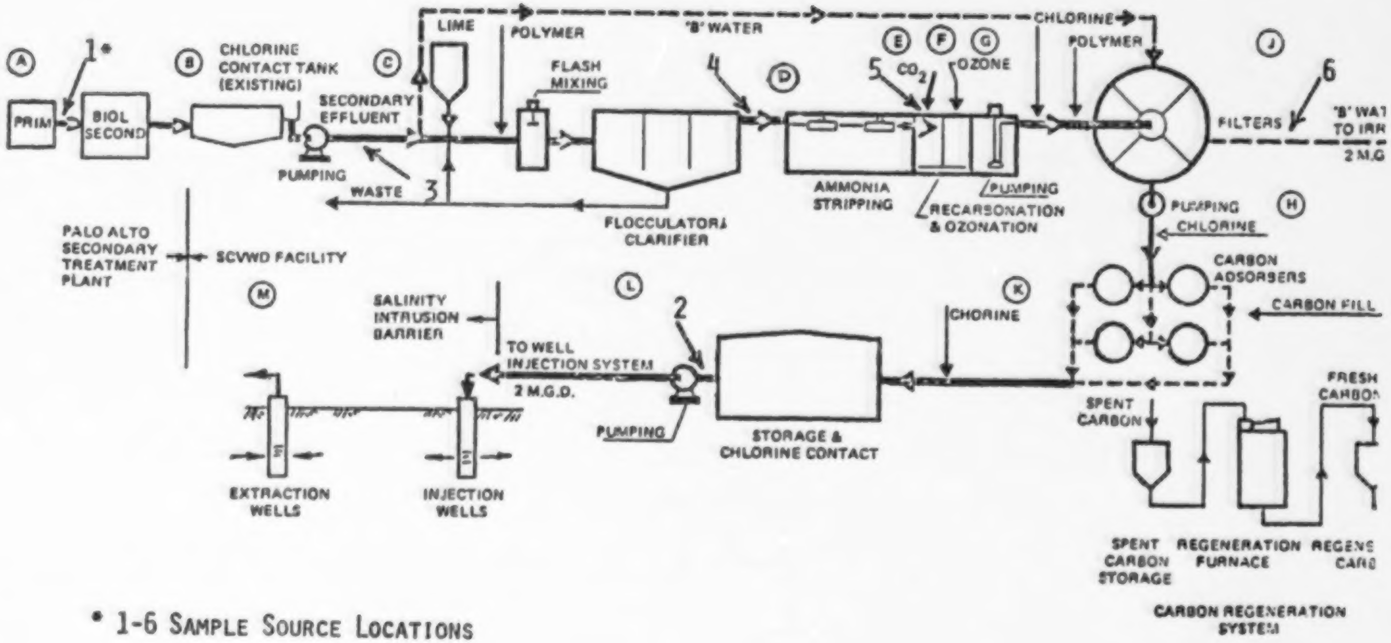
Gas Chromatograph. The calibration methods and gas chromatographic separations require further refinement. Preparation methods for calibration mixtures need to be standardized in order to produce accurate and repeatable standards. Columns that will separate all of the chlorinated species of interest are also required. In addition, it would be desirable to expand the capability of the method to include analyses of important compounds such as benzene, toluene, chlorobenzene and dichlorobenzene which are not detected because of their poor response in the electron capture detector. The flame ionization detector has not worked due to high background noise from column bleed. A new column or more sensitive detector should solve this problem.

Future work would include decreasing the size of the system, decreasing the analysis time and expanding the capability of the system to analyze for other compounds.

SUMMARY

This summarizes the status for the WMS system including a brief historical background, results, and most important, the problems encountered in the project.

In spite of the difficulties, the experiences to date strongly suggest that the eventual success of this concept for automated water quality monitoring is certain. It is expected that by this time next year the current concept verification test phase will be complete. Definite recommendations for operational system design will be possible, and should include recommendations in the areas of increased sensor reliability, life, and sensitivity and operational procedures. Also, our partners in the test, SCVWD, will have enough data to evaluate the concept's utility for managing the operation of a wastewater reclamation facility, and make decisions on instrumenting their facility with similar instruments.


A
1*
PRIM
BIOL SECOND
B
CHLORINE CONTACT TANK (EXISTING)
C
SECONDARY EFFLUENT
PUMPING
WASTE
3
LIME
POLYMER
FLASH MIXING
FLOCCULATOR/ CLARIFIER
'B' WATER
4
D
AMMONIA STRIPPING
E
F
G
5
CO_2
OZONE
PUMPING
RECARBONATION & OZONATION
CHLORINE
POLYMER
J
FILTERS
6
'B' WAT TO IRR 2 M.G
PUMPING
CHLORINE
H
CARBON ADSORBERS
CARBON FILL
K
CHORINE
FRESH CARBON
SPENT CARBON
SPENT CARBON STORAGE
REGENERATION FURNACE
REGENE CARB
CARBON REGENERATION SYSTEM
STORAGE & CHLORINE CONTACT
2
L
PUMPING
TO WELL INJECTION SYSTEM 2 M.G.D.
SALINITY INTRUSION BARRIER
M
PALO ALTO SECONDARY TREATMENT PLANT
SCVWD FACILITY
EXTRACTION WELLS
INJECTION WELLS

* 1-6 SAMPLE SOURCE LOCATIONS

Figure A-1. Flow diagram SCVWD AWT facility

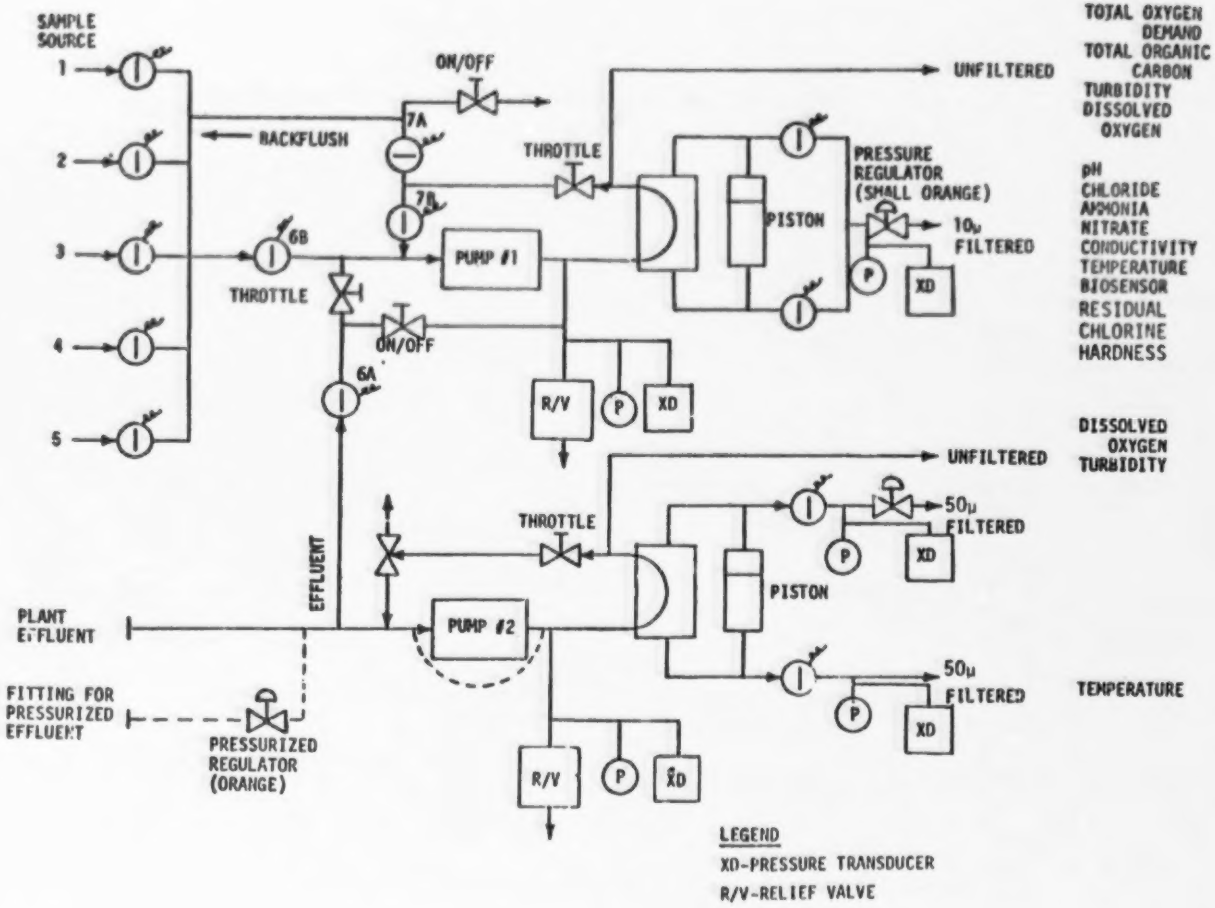

SAMPLE SOURCE
1
2
3
4
5
BACKFLUSH
ON/OFF
7A
7B
6B
THROTTLE
6A
ON/OFF
THROTTLE
PUMP #1
R/V
P
XD
UNFILTERED
PISTON
PRESSURE REGULATOR (SMALL ORANGE)
10μ FILTERED
P
XD
TOTAL OXYGEN DEMAND
TOTAL ORGANIC CARBON
TURBIDITY
DISSOLVED OXYGEN
pH
CHLORIDE
AMMONIA
NITRATE
CONDUCTIVITY
TEMPERATURE
BIOSENSOR
RESIDUAL CHLORINE
HARDNESS
UNFILTERED
DISSOLVED OXYGEN
TURBIDITY
THROTTLE
PISTON
50μ FILTERED
P
XD
50μ FILTERED
TEMPERATURE
P
XD
EFFLUENT
PLANT EFFLUENT
PUMP #2
FITTING FOR PRESSURIZED EFFLUENT
PRESSURIZED REGULATOR (ORANGE)
R/V
P
XD
LEGEND
XD-PRESSURE TRANSDUCER
R/V-RELIEF VALVE

Figure A-2. Sample conditioning and distribution

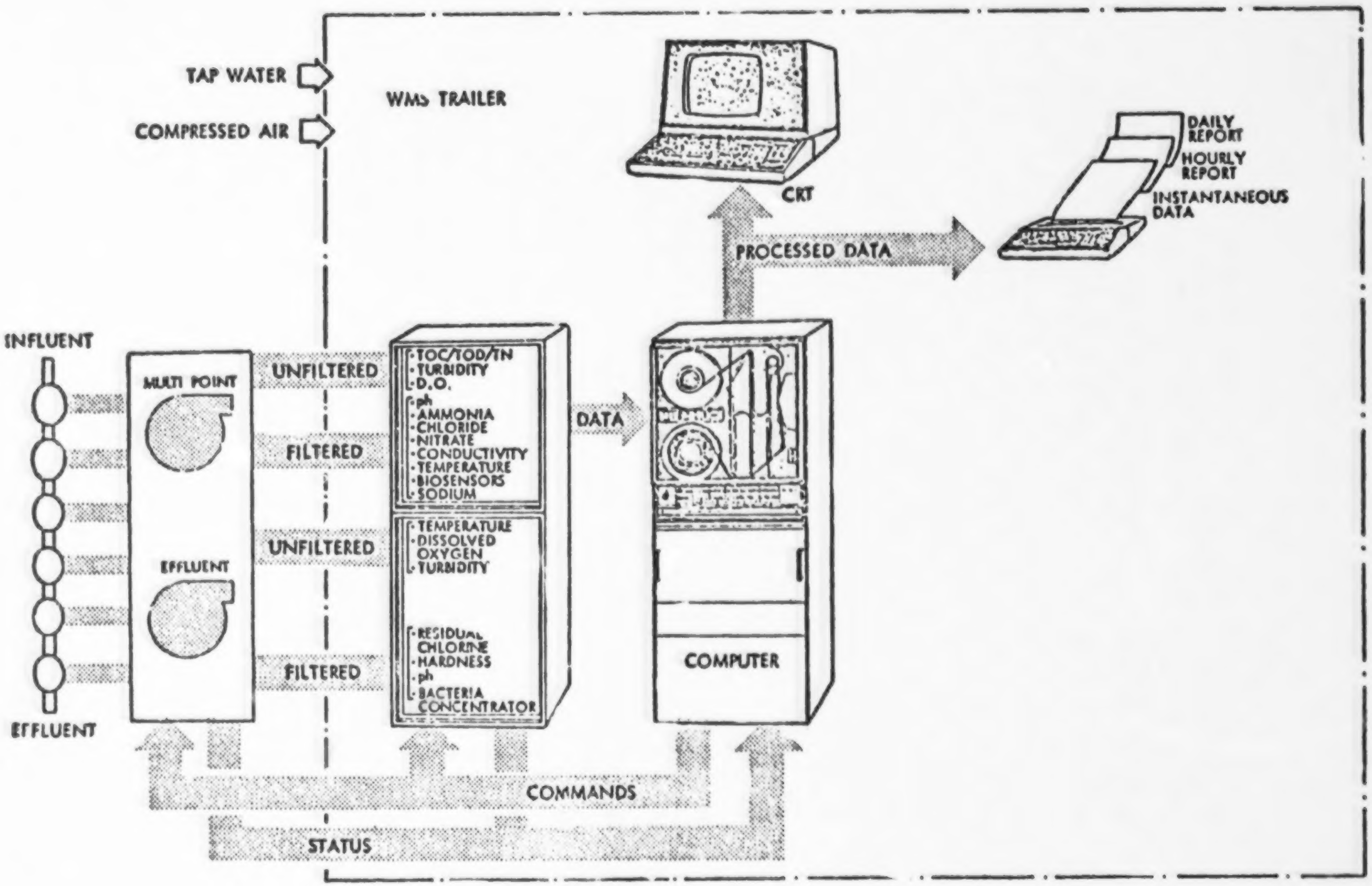

TAP WATER
COMPRESSED AIR
WMS TRAILER
CRT
DAILY REPORT
HOURLY REPORT
INSTANTANEOUS DATA
PROCESSED DATA
INFLUENT
EFFLUENT
MULTI POINT
EFFLUENT
UNFILTERED
FILTERED
UNFILTERED
FILTERED
·TOC/TOD/TN
·TURBIDITY
·D.O.
·ph
·AMMONIA
·CHLORIDE
·NITRATE
·CONDUCTIVITY
·TEMPERATURE
·BIOSENSORS
·SODIUM
·TEMPERATURE
·DISSOLVED OXYGEN
·TURBIDITY
·RESIDUAL CHLORINE
·HARDNESS
·ph
·BACTERIA CONCENTRATOR
DATA
COMPUTER
COMMANDS
STATUS

Figure A-3. Water monitoring system

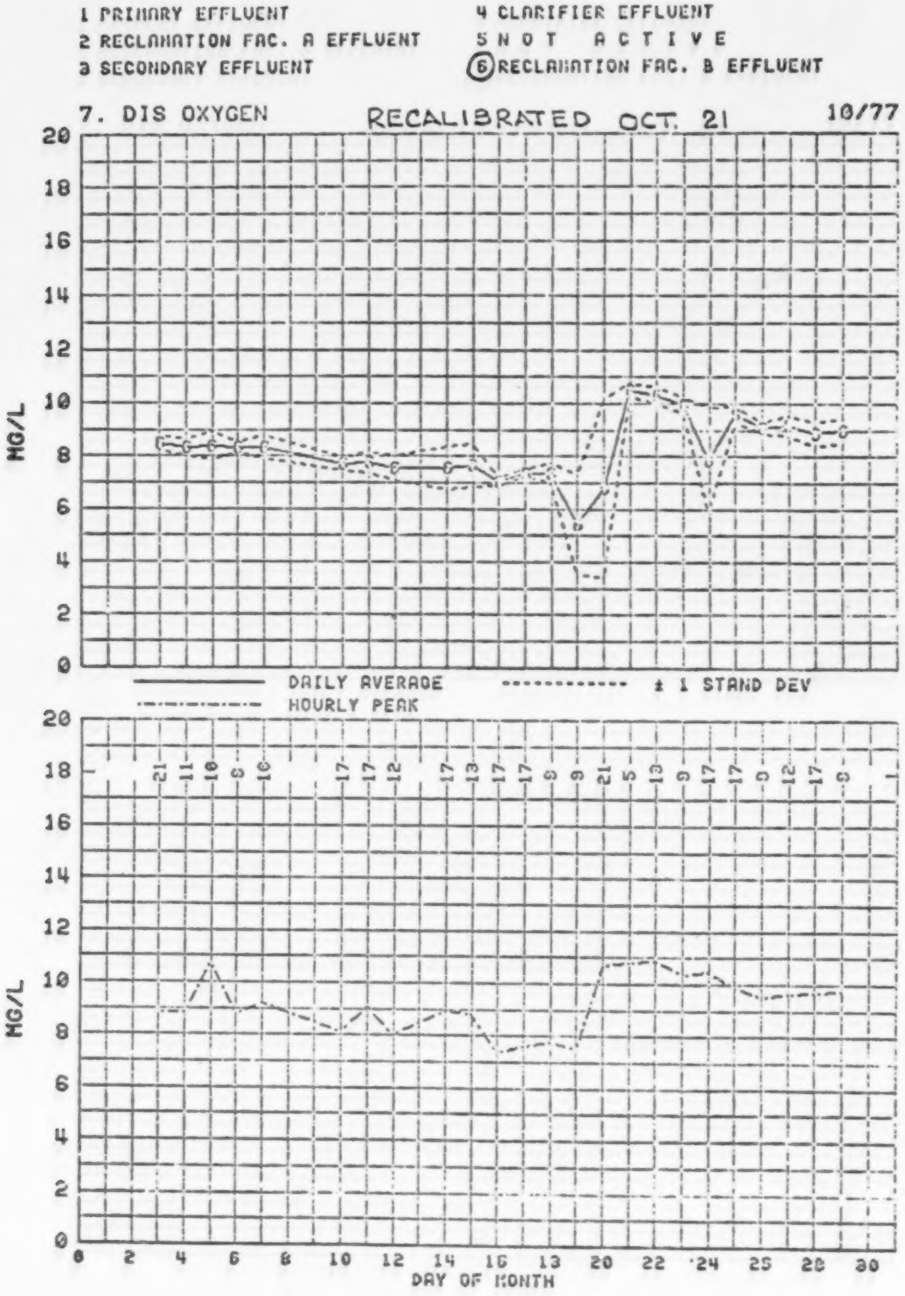


Figure A-4. NASA/WMS - SCVWD Palo Alto water reclamation facility

TABLE A-1 . TYPICAL DAILY DATA

	Reclamation Facility			
	Influent Avg. ± Std. Dev.	Config. *	Effluent Avg. ± Std. Dev.	% Reduction
Viable Biomass, cells/ml x 10^6	97.5 ± 42.7	1	4.5 ± 1.9	95.4
		2	0.3	99.7
Total Biomass, cells/ml x 10^6	177.6 ± 62.3	1	7.0 ± 3.3	96.7
		2	2.8	98.4
Fecal Coliform	-	3	0	-
t-Dichloroethylene, ppb	341.4	4	41.1	88.0
Chloroform + Methyl Chloroform, ppb	750.9	4	43.9	94.0
Trichloroethylene, ppb	109.7	4	18.2	91.3
Bromodichloromethane, ppb	4.2	4	0.2	95.2
Tetrachloroethylene, ppb	70.4	4	8.6	87.8
Turbidity, MG/L SiO_2(25°)	25.9 ± 5.5	1	18.4 ± 3.4	29.0
		2	15.1	41.7
Turbidity, NTU (90°)	7.2 ± 1.4	1	5.7 ± 1.9	20.8
		2	1.2 ± 0.1	83.3
Total Organic Carbon, ppm	47 ± 4	1	43 ± 5	8.5
		2	27	42.6
Ammonia, ppm	40 ± 5	1	31 ± 2	22.5
Dissolved Oxygen, ppm	3.7 ± 0.4	1	9.1 ± 0.4	-

(Continued)

TABLE A-1. (Continued)

	Reclamation Facility			
	Influent Avg. ± Std. Dev.	Config. *	Effluent Avg. ± Std. Dev.	% Reduction
Total Residual Chlorine, ppm	-	1	2.8 ± 0.6	-
pH	7.1 ± 0.1	1	7.3 ± 0.2	-
Conductivity, MHO/CM	1505 ± 23	1	1455 ± 40	3.3
		2	1375	

* 1 - 10-27-77, Flocculation, ammonia stripping, recarbonation, ozonization, chlorination

2 - 10-27-77, same as above with filtration

3 - 10-25-77, same as 1

4 - 10-19-77, same as 1

APPENDIX B. ELECTROCHEMICAL METHOD TO DETECT COLIFORM BACTERIA

The Federal Water Pollution Control Act of 1972 provides NASA with the charter to apply technology to monitor water pollution. Specifically, section 104 of this act charges the Environmental Protection Agency (EPA) to provide a water quality surveillance system for monitoring the quality of the navigable waters, groundwater, the contiguous zone, and the oceans. In order to aid in providing such a system, the EPA is charged to utilize the resources of NASA, to the extent practicable.

For the past 3 years research has been underway at the Langley Research Center to develop an automated in situ coliform monitoring system. The electrochemical sensor used to detect coliforms* was developed by Wilkins and Stoner. (1) The technique was based on measuring the time of hydrogen evolution as a function of inoculum size. A linear relationship was established for this parameter. A prototype system for monitoring levels of fecal coliforms was evaluated in both fresh water and established fecal coliforms. These evaluations were performed in conjunction with EPA Region II. Thirty-two samples were processed by the in situ electrochemical system during the evaluation. Correlation with laboratory standard methods for determining fecal coliforms was good for 14 samples, fair for 8 samples, poor for 6 samples, and undetermined for 4 samples due to faulty electrodes and insufficient laboratory data. As a note of explanation for these qualitative judgements, 'good' indicated that the laboratory data were within the range of the predicted values, 'fair' results had differences by a factor of 10 to 100, and 'poor' results had differences greater than 1000.

One important aspect is the relationship between in situ predicted coliform counts and the values obtained with conventional laboratory techniques using the Most Probable Number (MPN) of Membrane Filtration (MF) method. There is a fundamental difference between the two methods, viz., the electrochemical technique is based on a graded or 'time to response' relationship while conventional procedures are quantal or all-or-none observations. (2) In addition to these differences, the eventual use of the data from the two methods also differs. For example, MPN or MF results are used to determine the sanitary quality of the water for consumption, bathing beaches, etc. Coliform values beyond those prescribed by law result in condemnation procedures. In its current state of development, the electrochemical method cannot be viewed in the same light as the MPN or MF procedures. Rather, its explicit application in the in situ system was for monitoring the degree of contamination at the test site. On that basis, the in situ response times were arbitrarily divided into the following groups depending on the degree of contamination: detection time endpoints between 3 and 6.5 hours would be indicative of heavy contamination (400 to 6,000/100 ml), response times in the range of 7 to 10 hours would be moderate (25 to 250/100 ml), 10.5 to 14 hours would indicate light contamination (1 to 15/100 ml), and over 14 hours would indicate fairly low levels of fecal coliform contamination. The results obtained during the field evaluation would tend to support these arbitrary designations. For example, base station response times at Caven Point, New Jersey, were approximately 6.5 hours which indicated heavy pollution. This was in agreement with the mean laboratory fecal coliform counts of 633/100 ml. On the other hand, base station response times at the York River deployment were extended (12 to 17 hours), indicating light contamination. This was also in agreement with mean laboratory fecal coliform values of 27/100 ml.

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*Coliforms are the principal biological indicators of the sanitary quality of water.

The concept of remotely monitoring the levels of fecal coliforms with the electrochemical method was verified although utility of the in situ system would be limited to specific ecological situations. It appeared that the in situ concept would be most useful in defining areas heavily contaminated with fecal coliforms. Placed in clean areas suspected of receiving large amounts of pollution, the system could be utilized as an 'early warning' of impending contamination. Based on the limited data and experience obtained during four deployments, the in situ sampler has to be viewed as a monitoring system rather than a system to obtain precise measurements to meet regulatory requirements.

Based on extensive experience, it was felt that the primary reason for the 'poor' and to some extent the 'fair' in situ results was due to the combination redox electrodes. As described by Wilkins et al. (3) the electronic sensing of an endpoint consisted of detecting two levels of response, 30 and 90 millivolts. Inherent in this requirement is a steady baseline. Any drifting will cause an early 'triggering' of the electronics resulting in a false positive response. In addition, if the required millivolt response levels are not reached, the electronics will cycle in an attempt to locate the proper levels. Numerous tests have failed to identify the source of these anomalies. The questionable reliability of the combination electrodes precludes their use in future in situ systems. In an attempt to circumvent this problem area, investigations are underway to develop electrodes of a simple design with high reliability. Stoner has shown that electrodes of similar metals could be used to detect bacteria providing one of the electrodes was shielded from the organisms. (4) This work was funded by EPA and monitored by NASA. Wilkins has demonstrated the efficacy of platinum electrodes in which both electrodes could be in contact with the bacteria providing that a surface area ratio of four to one was maintained. (5) Future applications of the in situ concept will incorporate one of these electrode designs.

The following general conclusions were reached after reviewing the data obtained during four deployments of the in situ coliform monitoring system. There were a number of features associated with the current design of the in situ system that restricted its general utility. For example, in view of the size and weight of the system, deployment and retrieval required experienced 'riggers' and the use of a heavy duty, mobile crane. The 'batch' design limited the number of samples that could be processed to 10. If the unit was located in water temperatures of $\leq 8.0^{\circ}$ C, the power requirements on the batteries to maintain a water bath temperature of 44.5° C restricted deployment time to less than 10 days. As discussed previously, the questionable performance of the combination electrodes distracted from the required reliability of the system. In view of these problem areas associated with a 'batch' system, the most promising future technology appears to reside with a flow-through system. The major advantage of a flow-through system would be the continuous processing of samples without the need for frequent refurbishment. Studies currently underway at the Langley Research Center indicate that daily samples could be processed for up to 6 months before the unit would be retrieved.

Very early in the development of the in situ monitoring system, an interagency agreement was developed between EPA (Region II) and NASA. Four tasks were delineated. One of these tasks detailed the conditions for a cooperative field evaluation of the in situ system at Caven Point, New Jersey. This agreement proved to be an excellent arrangement between the systems development agency, NASA, and the user agency, EPA. It provided NASA with the users requirements and at the same time afforded EPA the opportunity to become familiar with the system and its limitations. In addition, the interagency agreement also helped to prevent any possible duplication of research and development effort.

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APPENDIX C. MINIATURIZED ELECTROCHEMICAL AND IMMOBILIZED ENZYME SENSORS FOR IN SITU WATER QUALITY MEASUREMENT

During the past three years, research and development on sensors and techniques for in situ water quality monitoring was undertaken in the Chemical and Petroleum Engineering Department at the University of Pittsburgh under the sponsorship of NASA.* Efforts were devoted to the research on advanced electrochemical sensors and immobilized enzyme sensors for possible application to in situ water quality monitoring.

The sensors used in commercial water quality monitoring instruments, by and large, are all electrochemical sensors. For instance, dissolved oxygen, pH value and electrical conductivity detectors all employ electrochemical sensors. The measurements of chloride ions, ammonia and other chemical and biological parameters in water quality are also performed by electrochemical techniques. Hence, it is appropriate to devote research efforts to the development of electrochemical sensors for in situ water quality monitoring.

In situ measurements suggest the need for instruments that permit continuous, unattended monitoring of the essential environmental parameters quantitatively. To a lesser extent, in situ measurements also imply a mobile and portable instrument which is capable of detecting and identifying the pollutants in a quantitative manner. Hence, in situ water quality sensors should have good sensitivity, durability, reliability, minimum power consumption and small sample volume. In our laboratories, miniature pO_2, and pH sensors are developed based on the premises that miniature sensors may have the advantages of small sample volume and low power consumption. Consequently, they may be both portable and suitable for long-term in situ quality monitoring.

The operation of a miniature pO_2 sensor is based upon the polarographic principle. The gold cathode has a diameter of 0.127 mm (5 mil) and the anode is a sintered silver-silver chloride electrode, 2 mm in diameter and 3 mm long. A selective membrane is applied to the cathode to minimize ionic interference. The polarizing potential is 0.7 volt, and the limiting current, of the order of nanoamperes, is in direct proportion to the oxygen dissolved in the medium (water).

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*Work performed under NASA Grant NSG-3002. Principal Investigator, Chung-Chiun Liu, Professor, Chemical and Petroleum Engineering Department, University of Pittsburgh.

A miniature glass pH electrode was developed, fabricated and evaluated. Hydrogen ion-sensitive glass (Corning 015) is used in constructing the electrode. The inner electrolyte is a 0.1 N HCl solution and the inner reference electrode is an Ag/AgCl electrode, 0.127 mm in diameter. The average tip thickness of the electrode is 0.484 mm compared to a wall thickness of 0.25 mm. An integral circuit field-effect-transistor (FET) input operational amplifier is incorporated into the pH electrode to widen the effective range of measureable pH values.

These miniature pO_2, pH sensors have been used in field tests and have been incorporated into a portable water quality monitoring system. Limited field testing has demonstrated the feasibility of using such sensors for in situ water quality monitoring.

In addition to the research efforts on advanced electrochemical sensors, our other research efforts are focused upon the development of immobilized enzyme sensors. Many enzymes are excellent catalysts for oxidation or reduction reactions for biological species. The high degree of sensitivity and selectivity of the enzyme in these reactions is impressive, and can be applied to in situ water quality monitoring. However, in order to use the enzyme repeatedly over a reasonably long period of time, the enzyme will have to be immobilized either by physical entrapment or chemical bonding techniques. This immobilized enzyme on a substrate can then be placed in the testing medium. The enzymatic reaction, if coupled with a redox reaction of electrochemically active species, will result in a measurable electrochemical potential. This zero-current potential is Nernstian in nature, and exhibits a linear relation with respect to the logarithmic values of the concentration (activity) of the detecting substrate. Based upon this concept, immobilized enzyme sensors are being developed in our laboratories. Efforts have been devoted to the studies of enzyme immobilization techniques and applications of enzyme sensors to in situ water quality monitoring. Specifically, a phenol sensor has been developed, and the possibilities of using enzyme sensors for trace metal monitoring are being investigated.

The phenol sensor incorporates the enzyme phenol oxidase (tyrosinase), immobilized within a polyacrylamide gel, into an electrochemical system for phenol detection. Coupled with the oxidation of ferrocyanide ions to ferricyanide ions and using potentiometric techniques, the phenol sensor is capable of producing aero-current potentials that are directly proportional to the logarithm of phenol concentration over the range of 3.8×10^{-7} M to 1×10^{-4} M. Although this sensor does not provide the greatest sensitivity available to detect phenol and related compounds, it does provide accurate and reproducible measurements which can be made on a continuous basis. Furthermore, introduction of the sensor into the text medium is a simple process. Once operating, the sensor response time is rapid, on the order of 10 minutes or less.

Biochemically, phenol can be oxidized by oxygen in the presence of the enzyme tyrosinase, to 1, 2 dihydroxybenzene and then to orthobenzoquinone. When the reaction proceeds in the presence of potassium ferrocyanide, the ferrocyanide ions are oxidized to ferricyanide ions with the concurrent reduction of the orthobenzoquinone to 1, 2, dihydrozybenzene. Thus, the oxidation potential of ferrocyanide ions can be used as an indication of the phenol concentration.

The performance of this phenol sensor has been evaluated in terms of its calibration characteristic, reproducibility, performance affected by oxygen concentration, performance in the presence of phenol analogs, etc. The actual response of the phenol sensor has also been evaluated by using industrial effluents. An arrangement was made with Mobay Chemical Co., Pittsburgh, Pennsylvania, to test their effluent samples. Mobay Chemical took seven effluent samples and divided each sample into portions. One portion of the sample was analyzed by Mobay using a chemical colormetric method. The other portion of the sample was analyzed in our laboratory using the immobilized phenol sensor. We had no prior information on the phenol concentration in each sample and our analytical results were reported to Mobay for comparison. The comparative results show:

TABLE C-1. PHENOL CONCENTRATION, PPM

Sample No.	Our Method	Mobay
1	2	6
2	--*	0.005
3	--*	0.027
4	0.3	0.48
5	1.0	5.25
6	80.0	87.5
7	<3	0.01

*Undetectable

In general, the results of the immobilized enzyme phenol sensor are very close to those obtained by Mobay. Also, the analysis procedure is simple. We are in the process of developing a prototype sensor for in situ automated water (industrial effluent) quality monitoring.

Another research area on immobilized enzyme sensors concerns the applications of enzymatic reactions for trace metal analysis. Many enzymes have been known to be highly sensitive to heavy metal ions. Analytical methods for determining trace metal ions based upon their inhibition in enzyme reactions have been demonstrated. In general, the initial rate of an enzyme reaction will decrease with increasing inhibitor concentration. The range of this linear region depends on the nature of inhibition; that is, whether it is reversible or irreversible.

Based upon this principle, it is feasible to use the inhibition effects of heavy metal ions on selected enzyme reactions as a means for monitoring the heavy metal ions. It is anticipated that the presence of other heavy metal ions may cause interference in the detection. This interference may be alleviated by applying sample separation techniques or masking procedures.

The enzyme used in this study is immobilized in polyacrylamide gel over a platinum screen, in order to increase its stability and reuse. This enzyme-gel platinum matrix (sensor) is then used in conjunction with a redox reaction of electrochemically active species. The zero-current electrochemical potential produced due to this coupled redox reaction is used as the measuring output of the detection. The rationale of choosing this mode of operation is based on the successful development of phenol sensors described above. Other measuring techniques such as ampermetric measurement, pH value change, pO_2 consumption, etc., can also be considered as an alternative mode of operation.

At present, the inhibition effects by heavy metal ions on enzymatic reactions is studied using the xanthine oxidase system. This enzyme catalyzes the oxidation of hypoxanthine and xanthine. The inhibition effects of heavy metal ions on this enzyme reaction are currently being investigated as the means to quantify the heavy metal ions presented. This approach is novel and also requires very simple instrumentation. Consequently, this technique may be applicable to the in situ water quality monitoring.

In summary, our research efforts on sensors for in situ water quality monitoring are devoted to advanced electrochemical sensors and immobilized enzyme sensors. We hope the development of miniature, low power requirement sensors would permit long-term, durable and highly sensitive in situ monitoring. Also, the development of highly-selective enzyme sensors would lead to minimum interference, simple instrumentation and highly-sensitive detection of essential chemical and biological water quality parameters. We believe that these research efforts would aid in the sensor development for in situ water quality monitoring and yield substantial results in the near future.

APPENDIX D. OTHER ACTIVITIES WITHIN NASA

The Instrumental Detection of Viruses is being investigated for EPA at the Jet Propulsion Laboratory for use in monitoring environmental conditions at sewage processing facilities. A laboratory facility has been established to develop the appropriate instrumentation and feasibility has been demonstrated. Further developments are continuing to increase the effectiveness of the system. The technology is based upon tunable accoustical-optical filters derived from the space program.

A Neutron Gamma-Ray Detection and Monitoring System is being developed at Goddard Space Flight Center for use in analysis of the superficial layers of the sea bottom, water quality and water pollution. A prototype has been demonstrated. A system is being designed for use in surface and submarine vessels for evaluation in the ocean and rivers in the summer 1978. The technology is based upon that used in remote analysis of the lunar surface physical properties. The radiated material yields a signature which can be analyzed by a computer to identify the chemical properties. This project is a joint effort with DOE, EPA, NOAA and USGS.

A Thermal Plume Monitoring System is being developed for NOAA at the Langley Research Center for use in giving temperature depth profiles in thermal plumes from power plants and ocean thermal movements. The acoustic bathythermograph was demonstrated and redesigned to overcome deficiencies. Another demonstration is planned in the spring 1978. The technology is based upon some variations with temperature. The inexpensive and miniature sensors permit deployment from ships of opportunity to map ocean thermal profiles.

Acoustic Tracking of Woodhead Sea Bed Drifters was developed for NOAA at the Langley Research Center in 1975 on a demonstration cruise in the New York Bight. It was concluded that shipboard sonar tracking of acoustic woodhead sea bed drifters could provide useful Lagrangian information on bottom water movement caused by tidal and other nonstorm effects. A NASA Technical Note NASA TN D-8392 has been published.

A Portable X-Ray Fluorescence Spectrometer is being developed at the Langley Research Center for use in water pollution analysis (trace metals), oil analysis (metal contaminants), energy resource exploration (uranium core analysis) and fuel contaminant analysis (sulfur in coal). The first prototype is to be demonstrated in August 1979 for use by the Bureau of Mines to assist in determining the bearing strength of mine walls, for obtaining higher yields from ores in mining operations and to minimize sample selection and analysis from field exploration in wilderness areas. The design is a modification of that employed in the Viking spacecraft for analysis of Martian soils.

An Implantable Acoustic-Beacon Automatic Fish Tracking System has been developed for the Virginia Institute of Marine Science at the Langley Research Center. The system was demonstrated in the York River where pingers were implanted in small fish and were successfully tracked up to 2.5 km. No changes in either fish behavior or pinger performance were observed. The system is commercially available and provides an effective approach to underwater tracking of small fish within a fixed area of interest. A NASA Technical Note (NASA TN D-8498) has been published. The purpose of this effort was to investigate the effects on fish of man-made perturbations in estuarine waters.

NATIONAL BUREAU OF STANDARDS

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The mission of the National Bureau of Standards is to provide standards of measurement and means for making measurements consistent with these standards and to provide physical constants and properties of materials. To this end, the major products of the NBS Water Measurement Program are measurement standards, measurement methods and evaluated and improved data for relating effluents to ambient water quality. Thus, in terms of water quality sensors, NBS is concerned with the reliability and accuracy of specific types of sensors, with the possible development of new sensors and with the study of properties which may have some application to sensor design. NBS does not have monitoring responsibilities and hence must turn to the monitoring community for guidance on measurement method needs.

As already mentioned, the major products of NBS efforts are measurement standards, measurement methods and evaluated data for describing the distribution of substances in water. The measurement standards include standards for the measurement of chemical constituents in water and the measurement of water flow.

Standards for the measurement of the chemical constituents in water can be check samples for interlaboratory comparisons or NBS Certified Standard Reference Materials (SRM's). SRM's are materials whose selected properties have been accurately measured and certified. They can be used to evaluate measurement methods and can serve as a basis for validation, through carefully documented comparison of working, reference or calibration standards. To date the NBS Office of Standard Reference Materials has issued and sold mixed gamma-emitting radionuclide solution standards; two mercury-in-water standards (one at the ppm concentration level and one at the ppb concentration level); a multielement standard consisting of 16 elements in the concentration range of 1 to 100 ppb with sodium, potassium, magnesium, and calcium added at the ppm level to simulate a natural fresh water sample; and a sediment standard certified for the radioactivity. A sediment standard certified for trace element composition as well as total Kjeldahl nitrogen, phosphorous, total organic carbon and loss on ignition will soon be offered. Check samples are generally developed for other Federal Agencies for the purpose of testing laboratory performance. These standards are not subjected to the same rigorous certification procedures as SRM's and, because they are intended for use not long after they are prepared, they do not receive the same stability testing as SRM's. Examples of such check standards have included solutions with known radioactivity levels, synthetic rainwater samples, solutions of polynuclear aromatic hydrocarbons in organic solvents, phenols in organic solvents and water, sediment samples and biological samples.

NBS scientists are also engaged in the development of standards for water flow and the development of means for allowing flow measurements to be compared with these standards. The standards will consist of a closed circuit water tunnel in which turbulence and wall effects can be predictably controlled and an open channel facility with known flow. With these two standards, common methods for flow measurement can be evaluated and sources of error identified and quantified. The means for ensuring comparability of field measurements to these standards will consist of mathematical models and accompanying guidelines. With the guidelines, field engineers can measure prescribed geometries and velocities as well as noting installation conditions, and consulting engineers can analyze the observations with the mathematical models to provide calibration of the installation.

As already mentioned, another portion of the NBS mission is the determination of physical and chemical properties of materials and the development of methods for measuring these properties more accurately. Research activities applicable to water monitoring problems include the measurement of those properties affecting the fate and distribution of chemicals in the environment and the studies of properties which relate to analytical chemical methods. Properties affecting the distribution and fate of chemicals in the environment include solubility; partition coefficients, adsorptivity and chemical stability (including photochemical stability). Properties which relate to analytical determination of compounds in water include activity coefficients (for electrochemical response), partition coefficients (for separation efficiencies), membrane permeability, surface chemistry and spectra. It is in the provision of Standard Reference Materials for the evaluation of sensors and in basic research into the properties of materials as they relate to the measurement process that NBS can be expected to make its greatest contribution to the development of in situ water sensors.

U.S. NAVY, OFFICE OF NAVAL RESEARCH

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The Geography Program of the Office of Naval Research has been conducting research in remote monitoring as it might apply to aiding in the prediction of changes in conditions of coastal environments.

The remote monitoring program is concerned with determining the feasibility of using various sensors to acquire accurate and timely measurements of significant diagnostic parameters. Particularly, the program is dedicated to understanding the physics producing and affecting the energy signals received and recorded by the various sensors.

Our main concerns have been and are attempting to acquire bathymetric data rapidly and accurately, in determining temperature and salinity as a function of depth, and in general determining the normal distribution of bioluminescent and fluorescent material in the world ocean. None of the research dealing with these projects has been concerned with water quality per se, but one can easily surmise that a spin-off from these projects could be a capability to predict water quality from remotely sensed data.

Our bathymetric studies have included the use of lasers, cameras, and a multispectral scanner. We are actually dealing with water turbidity when attempting to acquire bathymetric data.

Preliminary experiments have shown that there is a direct correlation between the amplitude and shape of the elastic (no change in wavelength) laser backscattered signal and water turbidity. These experiments showed a linear relationship between the magnitude of the laser backscatter and turbidity. Although this relationship was found to exist at all wavelengths, the greatest effect occurred for a laser excited wavelength of 440 nm. These preliminary measurements indicate the feasibility of using the backscatter from an airborne laser transceiver as a direct-reading alphameter (sediment load). The accuracy of this technique for measuring alpha at 440 nm is estimated to be 5 to 10 percent.

A second method for determining water turbidity proved successful; this method consisted of using the measured intensities of subsurface reflections, determined for two water depths, to yield the effective attenuation coefficient of the water.

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* This narrative not presented orally at the Workshop.

A third method consisted of using a pulsed laser to excite fluorescence in a dye cloud, which was composed of more than one dye. The peak fluorescence signals from the multiple dyes are detected. Ratioing techniques are then used to extract various hydrographic parameters, such as water depth, temperature, salinity and water turbidity, from the data.

Detailed analysis of the inelastic Raman backscattered signal from the water should be able to provide one with a value of the water turbidity in a manner similar to that using the laser elastic backscatter signal. It has been shown that selective signatures can be obtained utilizing Raman and Fluorescent Spectroscopy. This high degree of selectivity which is obtainable using these technologies results from the fact that the intensities and wavelength of emissions from a particular material are directly coupled to the intensity and wavelength of the source of illumination. This therefore enhances the probability of being able to detect and identify specific material in the water.

Remote sensing of fluorescent matter either floating on the water or within the water column may yield information on existing currents and eddies at various water depths. Since temperature and salinity affect the intensities and spectral character of the fluorescent and Raman signals, it is possible that remote detection of these signals can be used to measure these quantities as well as turbidity.

The possible use of fluorescence as an indicator of subsurface disturbances is given by the following example: The majority of the upper ocean is thermally stratified, sterile and blue in color. When this stratification is overturned as by natural currents, human activity, and/or meteorological events, nutrients and cold water are transported into the sunlit layers.

Our research program is concerned with all the in-situ and remote sensing data obtained in the past on naturally occurring matters such as gelbstoff, bioluminescence and phytoplankton. The investigation also includes the assessment of research programs which have been involved with the nature and distribution of other organics which under the right conditions might fluoresce. In addition, this program is considering the signatures and sensitivities of measuring equipment to interferences due to fish fluorescence and that due to accidental or planned oil releases. The results of this program will be used to assess the feasibility of using fluorescence, and possibly Raman signatures, of material in the water as indicators of various parameters, temperature, salinity, etc., in the hydrosphere. The results of this study will also be useful in guiding future research efforts in the measurement and prediction of the fluorescent material in the waters of the world.

The Over-the-Horizon (OTH) drogue system consists of a low cost, expendable sea sonde that can be used with OTH in either the ground wave or sky modes to obtain real time coastal and oceanographic data. Data that can now be obtained include wave height and period, temperature and salinity as a function of depth, current direction and speed as a function of depth, turbidity, chemical oceanography, and meteorological measurements.

The OTH/drogue system is already being utilized by industry and various government agencies. Further development is needed to make the system air-droppable and self-mooring, to add to the system capabilities, and to bring it into operational readiness for the Navy. This OTH/drogue capability will be part of the coastal reconnaissance system now being developed by the Navy and Marine Corps.

This extremely brief glimpse into some of our research in ONR Geography Programs serves to emphasize the importance of knowing the environment being sensed, knowing the characteristics of the sensor, and knowing when to use the sensor as well as how to process the data for various levels of analysis.

U.S. COAST GUARD

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Coast Guard pollution surveillance responsibilities can be traced back to the mid 1960's. The Federal Water Pollution Control Act (FWPCA) as amended in 1966, 1972, and 1977 set the parameters for such a surveillance system. One section of the Act calls for the preparation and publication of a National Contingency Plan (NCP) for the removal of oil and hazardous substances. This legislation mandates that the NCP include:

> ". . . a system of surveillance and notice designated to insure earliest possible notice of discharges of oil and imminent threats of such discharges to the appropriate State and Federal agencies." (FWPCA, Section 311(c)(2))

The NCP qualifies the type of surveillance system required of the Coast Guard. Another section states, in part:

> ". . . the Coast Guard maintains continuously manned facilities that are capable of command, control, and surveillance for discharges occurring on the waters of the United States or the high seas." (MCP, Sec. 1510.22(i))

Research and development for aerial pollution surveillance sensors was initiated in 1969. It was soon realized that while similar principles could be employed, harbor surveillance called for different types of sensor applications. Research and development along this avenue began in 1971.

The Coast Guard is currently evaluating three types of water quality sensors on the Rouge River in Detroit, Michigan. This marine environment is known for its chronic pollution problems. The sensors are placed in strategic locations along the river which are historically known for oil spills and seepage. They are linked to Coast Guard Group Detroit by a communications system that employs both telemetry and a leased telephone line. The equipment undergoing testing includes the Spectrogram Ultraviolet Oil Detection Buoy (Spectrogram, Inc., North Haven, CT.), Rambie Infrared Oil Sensor (Rambie, Inc. Irving, TX.), and the Buoy Mountable Hydrocarbon Vapor Sensor (Midwest Research Institute, Kansas City, MO.). All three sensors have been previously employed in New York (Bayonne) or New Haven Harbors where they underwent initial testing.

Evaluative testing is proceeding satisfactorily and is scheduled to run through September of this year. Provided that no major problems materialize, plans call for placing another such sensor system in a saltwater port area in late 1978. The port/harbor chosen will have to be of medium size, have areas of chronic oil spillage, and have a Coast Guard Marine Safety office or Captain of the Port Office which utilizes a 24-hour watch. Two ideal possibilities that are under consideration are Baltimore and Houston. A final decision will be made later this year.

The environments under which these sensors have operated are quite varied. In all three areas, New York, Connecticut and Michigan, the equipment operated in temperatures which fluctuated anywhere between extreme heat (above 90° F) and extreme cold (below 0° F). The Rambie and Spectrogram sensors are not capable of detecting oil on ice. Oil must float past them for a programmed period so the equipment can compare what it "sees" to the background readings. The hydrocarbon vapor sensor can be employed to fill this void. Humidity has negligible effects on the sensors, however, in theory the range of Rambie's equipment should be affected by fog or heavy haze. To date, this situation has not been experienced. All three test areas are highly industrialized. Heavy air and water pollution exist. The Rouge River especially has been subjected to years of industrial abuse. The auto industry, among others, has used the river's waters as a sewer to deposit its industrial wastes. This condition, even today, goes virtually unchecked due to the industry's political and economic ties with the area. Detroit itself is honeycombed with a complex outfall system. Many times it is impossible to pinpoint a spill source after the pollutant reaches an outfall's mouth.

To cope with a wide range of environments, the Coast Guard requires sensors which are continuously monitoring, automatically resettable, self sustainable, low cost, low power, and able to detect, identify, and quantify oils and hazardous substances in harbors and inland waters. Though it is within the capabilities of these sensors to detect any visible sheen, this may be too sensitive from an operational standpoint. A visible sheen (1-3 microns in thickness) constitutes a violation of federal water pollution laws. In reality, this is unenforceable. In places like the Rouge River, sensor alarms would be triggered constantly. This is, in fact, what actually occurred immediately after the system became operational. Sensitivities had to be decreased. One way this conflict of interest can be approached is to place less sensitive sensors in chronic spill areas and, as the spill problems subside, slowly increase the sensitivities. This will, undoubtedly, have to be resolved in the near future.

Sensitivity is not the only problem inherent in an in situ sensor system. Another major problem experienced at the Rouge River test site is an inconsistent communications link between the sensors and display board (located at the Group Office). It was discovered that the source of the difficulties did not exist in the telemetry system between sensors and the leased telephone line as was originally thought, but in Michigan Bell Telephone Company's equipment. The leased line was inoperative for 3 months during the summer of 1977. Throughout this period, Spectrogram called Michigan Bell everyday without results. It was only after the contractor threatened suit that the telephone company repaired its equipment. Afterward, the system worked well for approximately one month, then the line became inoperative again and remained that way until the Spectrogram buoys were removed from the river for the winter. Present plans are to convert the telephone line to a more reliable teletype link.

Another problem that has been experienced may be related to the environment under which the sensors operate. The Rouge River winds its way through downtown Detroit where there are numerous tall buildings and industrial stacks. Transmission of sensor data in this environment is more difficult requiring more power to achieve clear transmissions. Larger power requirements lead to more solar panels and bigger batteries resulting in increased costs and weight. Most of this can be alleviated in a harbor environment as communications can take better advantage of an unrestricted line-of-site.

The Spectrogram buoys rely on solar energy to recharge their batteries and for power during daylight hours. The solar cells employed for this purpose have a 12-percent solar to electrical conversion. Vandals, on a number of occasions, have thrown rocks through the panels. Any small crack can effectively reduce panel efficiency by 2-3 percent placing a heavier load on the batteries. While not a system-related deficiency, it is one which must be coped with in any urban environment.

Industrial receptiveness is yet another source of problems. Many industries who are using the river to discharge industrial wastes see the sensors as a threat to this comparatively inexpensive practice. Faced with high treatment and/or disposal costs to remove these contaminants, several companies have not been receptive to Coast Guard requests to rent space on their property for test equipment. Some companies have been completely uncooperative, and on two occasions a Spectrogram buoy moored adjacent to a major motor company's outfall was sabotaged.

Probably the most important problem associated with these sensors is their limited field of view. They are spot sensors and, as such, if oil does not pass within their scope they cannot possibly detect it. To alleviate this, Rambie, Inc., is incorporating a scanning feature into their models. In the case of the hydrocarbon vapor sensor, deficiencies lie in the alarm and logic circuits. Additional work is needed in this area to make this sensor ready for operational use.

As was mentioned before, sensor sensitivity is a problem. Rouge River water contains a high percentage of oil. The sensors are constructed in such a manner that, once in operation, they will adjust to a background value over an 8-hour period and use this as a standard to evaluate what it sees. When the background reading is high, as on the Rouge, the sensor may actually be seeing oil but not alarm.

Coast Guard research and development (R&D) in the field of in situ sensors has centered upon the current Rouge River test and improvements of that system. Spectrogram is looking into a better data communications system while Rambie has developed a small, low cost oil spotter and a scanning version of its infrared sensor. While one type sensor may be used to detect all types of oil, preliminary R&D indicates that this is not the case for hazardous substances. Different chemical groups require different technical applications for detection. R&D is continuing in this field.

Coast Guard opinion dictates that while the basic principles behind infrared and ultraviolet oil detection will not change, future technology will center upon refining those sensor systems the Coast Guard already has. This will most likely involve creating sensors which have a larger effective field-of-view and more efficient telemetry and data communications systems. Quantification and positive identification of oil type might also be within the realm of future technology. Deepwater ports and other offshore facilities which employ underwater pipelines have inherent oil detection problems. Pipeline surveillance is currently conducted using flow meters (volume in, volume out). Future technology in this area could be applied in building better flow meters or developing a sensor which is capable of doing the same job more efficiently. A major consideration for the latter is the use of ultrasonic sensors. These would be employed at strategic locations along a pipe to listen for fluid leaks or metal stress.

The Coast Guard is not alone in its developmental efforts of water quality sensors. Both the Environmental Protection Agency and the Department of Energy have complementary programs in this field. While the Coast Guard has sponsored the Rouge River tests, these agencies have provided the bulk of the funding.

In situ sensors may be, at least, a partial solution to the momentous problem of water quality surveillance of ports, harbors and inland waters. In the year that they have been present on the Rouge River, a marked decrease of oil in river water has been noted. As was mentioned in the test, they do have a deterrent effect on industry. This alone may, in part, help to justify their existence. While still an operational concept of the future, in situ sensors are fast becoming a viable surveillance means of the present.

U.S. GEOLOGICAL SURVEY

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The Geological Survey's Water Resources Division conducts hydrologic programs to acquire, analyze, process, store, and disseminate data and information on the quantity, quality, location, movement, and changes in the Nation's water resources. The formal mission statement for the Water Resources Division is enclosed as Appendix A.

The Survey, as the principal Federal water data agency and as delegated by the Department of Interior, under OMB Circular A-67, has established the Office of Water Data Coordination (OWDC), which is charged with coordinating water data acquisition activities of all Federal agencies. OWDC develops regional and national plans for water data acquisition and has developed the "National Handbook of Recommended Methods for Water Data Acquisition," which has been compiled with the cooperation of experts from numerous Federal and non-Federal agencies. OWDC has constituted two standing advisory committees, one representing the private sector and one representing the Federal establishment, to enhance water data coordination.

The Geological Survey routinely collects data on river discharge, lake and reservoir content, surface and subsurface water quality, and groundwater levels at almost 40,000 separate sites. Approximately 25 percent of these stations have continuously operating unattended sensors. For example, over 9,000 stations continuously monitor and record river or reservoir levels in machine readable form, of which over 125 stations transmit their data by satellite retransmission for experimental evaluation of this technology. Several hundred stations monitor and record surface water quality.

In recent years, the Survey established the National Stream Quality Accounting Network (NASQUAN), which currently provides a uniform national network of 445 stations, which at its full design level will include 525 stations in Alaska, Hawaii, Puerto Rico, and the coterminous States. Information from this network is used to assess current water-quality conditions and trends. The bulk of the data collected at NASQUAN and other water-quality stations is derived from chemical, biological, and radiological analyses of routinely collected water samples. The Survey's field and project offices are served by two highly automated water-quality laboratories in Denver, Colorado, and Atlanta, Georgia, where analytical services and methods development are provided.

A key element in all Survey water resources programs is a computerized data base known as the National Water Data Storage and Retrieval System (WATSTORE). USGS offices daily and routinely enter, edit, process, and retrieve water data from WATSTORE files. Water-quality information for WATSTORE files is entered into the EPA STORET system, of which Survey data comprises almost half the data base.

The Survey's water resources activities are responsive to a combination of national and local needs--about half the support is provided by the Federal/State cooperative program, where funds are matched on a 50/50 basis by each party. Some 580 State and local agencies participate in the program. The remainder of the support is derived from Geological Survey budget line items and other Federal agencies.

The Survey's interest in water-quality sensors stems from the increasing need to collect continuous water-quality data nationwide. Water-quality sensors presently in use measure water temperature, pH, specific conductance at 25° C, and dissolved oxygen concentration. There are also a number of "turbidity" sensors in use; but, because of the difficulty in standardizing and defining the measurement of turbidity, the Survey is developing instrumentation for measuring light transmittance and scatter in water.

The Survey's network of hydrologic stations is national in scope, and the environment in which sensors must operate ranges from the tropical to the arctic. Some of the less obvious, but real, problems of the environment include risks of vandalism in urban and rural areas and the general difficulty of monitoring water in sand channel or ephemeral streams. For example, a large number of hydrologic stations are located on ephemeral streams where conventional stream gaging, sampling, and monitoring techniques are not effective. In such an environment, virtually all the animal river discharge, sediment load, and constituent transport occur during a few intense hydrologic events, which for logistical reasons are especially difficult for personnel to monitor. There are similar problems that are being encountered in a new program to monitor stormwater runoff in urban areas. In this program, measurements of discharge, precipitation, and water quality are made during a number of short duration intense events, where once again manual techniques are insufficient.

The Survey has developed and tested a variety of monitoring systems that support its programs. They include:

- USGS Water Quality Monitor. A ten-channel monitor designed by the USGS to operate off line power. There are about 85 monitors in operation in the field, with 50 new units under fabrication.

- USGS In Situ Water-Quality Monitor. A prototype four-parameter battery powered system is under test and is a scaled down version of the ten-channel monitor.

- USGS Urban Hydrology Monitor. An automatic system to monitor urban stormwater runoff. The system records precipitation and runoff and automatically collects samples, which are stored in a refrigerated chamber for later water-quality analysis. Nine prototype systems are in the field.

- Video Taping Hydrologic Events. This is a feasibility study to determine if video systems can monitor remote ephemeral streams to estimate discharge.

- Light Transmission-Scattering Meter. A prototype system is currently being tested. Further developmental work is planned for a system that can be used both in the field and the laboratory.

- Satellite Telemetry. Two potentially operational satellite telemetry systems are under test to monitor and collect data from hydrologic sensors.

The Survey participates in numerous interagency committees to coordinate water data collection activities. These include coordinating committees with NOAA, SCS, Fish and Wildlife, etc., as well as technology oriented groups, such as the Interagency Working Group on Satellite Data Collection Systems, which coordinates research in satellite telemetry technology. There is a need for additional ongoing and formal liaison between groups that are active in sensor development. The current workshop is a good opportunity to define the need and opportunity for coordination in water-quality sensor development.

APPENDIX A. U.S. GEOLOGICAL SURVEY, WATER RESOURCES DIVISION BASIC MISSION AND PROGRAM

The mission of the Water Resources Division is to provide the hydrologic information and understanding needed for the optimum utilization and management of the Nation's water resources for the overall benefit of the people of the United States.

This is accomplished, in large part, through cooperation with other Federal and non-Federal agencies by:

1. Collecting, on a systematic basis, data needed for the continuing determination and evaluation of the quantity, quality, and use of the Nation's water resources.

2. Conducting analytical and interpretive water-resource appraisals describing the occurrence, availability, and the physical, chemical, and biological characteristics of surface and groundwater.

3. Conducting supportive basic and problem-oriented research in hydraulics, hydrology, and related fields of science to improve the scientific basis for investigations and measurement techniques and to understand hydrologic systems sufficiently well to quantitatively predict their response to stress, either natural or manmade.

4. Disseminating the water data and the results of these investigations and research through reports, maps, computerized information services, and other forms of public releases.

5. Coordinating the activities of Federal agencies in the acquisition of water data for streams, lakes, reservoirs, estuaries, and groundwaters.

6. Providing scientific and technical assistance in hydrologic fields to other Federal, State and local agencies, to licensees of the Federal Power Commission, and to international agencies on behalf of the Department of State.

DEPARTMENT OF AGRICULTURE

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This report summarizes the experience of several USDA installations with regard to various types of water quality sensors. The experience summarized is from the USDA Science and Education Administration (SEA), formerly known as the Agricultural Research Service. Inquiries to the U.S. Forest Service and the Soil Conservation Service indicated a strong interest in such sensors but neither agency had initiated monitoring activities. Both agencies are desirous of feedback information from this workshop and both anticipate future application of remote water quality sensors to their missions.

The USDA is interested in (1) the quantity and quality of water available for agricultural activities and (2) the quality of the effluent from various agricultural activities which is passed downstream and affects those water resources. There is particular emphasis on nonpoint sources of potential water pollutants.

Within SEA there are four known locations where sensors are employed. The U.S. Salinity Laboratory at Riverside, California, has developed two different sensors for the purpose of measuring the salinity of soil moisture. These sensors are implanted in the soil and have a sensitivity of ± 1/4 to 1/2 millimhos/cm. Both sensors are marketed by commercial firms and are now employed around the world. They may be used wherever salinity measurements of soil moisture or groundwater are desired.

The USDA Water Quality Management Laboratory at Durant, Oklahoma, is utilizing sensors to monitor temperature, conductivity, dissolved oxygen, and pH in 10 model farm ponds, 6 meters in diameter and 2 1/2 meters deep. The water is fresh, eutrophic, and relatively stagnant. The sensitivities desired are all at one tenth of a unit and the present equipment is satisfactory from this standpoint at the time of calibration.

The temperature and conductivity sensors are working satisfactorily at Durant. The pH sensors require weekly calibration. The probes only last 6 to 9 months but the manufacturer has been replacing them at no charge. Currently available DO sensors will not maintain calibration more than a few days.

The USDA Southwest Rangeland Watershed Research Center at Tucson, Arizona, has employed conductivity and pH sensors for short durations. Performance has been generally satisfactory in an ephemeral environment.

An extremely sensitive sensor for measurement of specific density has been employed in the field at this location to continuously monitor suspended sediment in streams. This device is based on changing the resonant frequency of a vibrating tube when liquids of different densities flow through it. Performance of this sensor has been generally good.

This model density sensor has been used in the laboratory at the USDA Sedimentation Laboratory in Oxford, Mississippi, also with satisfactory results. Sixteen such units have recently been delivered to the Sedimentation Laboratory and will shortly be employed in a new research watershed study. Successful employment of these total solids resonance type sensors in the field study at Oxford, Mississippi, will be of great importance to our agency. The potential savings in labor compared to conventional sampling and traditional laboratory analytical techniques should be substantial. In this study research data will be collected by a line of sight radio communications system and acquired directly by the main laboratory computer.

The Sedimentation Laboratory also has eight automated water quality data collection stations located in the Mississippi Delta. These sensors are located in small streams and oxbow lakes with moderate suspended sediment loads. The drainage areas are almost entirely covered by row crops. Sensors employed include temperature, conductivity, DO and pH. Analog signals from these sensors are digitized and logged on magnetic tape cassettes. Automatic water sampling equipment is also employed to allow determination of water quality variables which are not determined by sensors.

Electromagnetic velocity sensors with no moving parts are employed to assist in the determination of water discharge. The velocity sensors have performed quite satisfactorily. One sensor has been used continuously in a polluted stream for almost 18 months without failure. Performance of the temperature and conductivity sensors has been satisfactory. Performance of the DO and pH sensors has been almost identical to that of the instruments at Durant, Oklahoma. We have been able to obtain satisfactory DO data only by servicing and calibration in the laboratory in the afternoon prior to field measurements the next day.

In SEA the most serious deficiency has been with the DO sensors. The problem seems to be one of poisoning of the membrane and the electrolyte solution. One suggestion may be to increase the volume of the electrolyte and modify the surface area of the membrane. New technology in the area of DO measurement would be very helpful. Field servicing and calibration is inconvenient, and faster and easier field calibration procedures should be sought.

During the past 5 years research has been conducted at the Sedimentation Laboratory to relate the spectral reflectance of solar energy from a water surface to some water quality variables, particularly inorganic suspended sediment. This work was initiated to provide ground truth for interpreting Landsat images and aerophotographs. A radiometer was used at water level and incident and reflected solar energy was measured at several wavelengths through the visible and near Infrared ranges. We have found very good relationships between a corrected reflectance in the range from 700 to 800 nanometers and the total suspended sediment load. A possibility exists for employing optical sensors to indicate other water quality variables. It should be emphasized, however, that optical sensors measure optical properties of the water which should only be used to interpret water quality variables after careful calibration.

The USDA Sedimentation Laboratory is presently cooperating with the U.S. Corps of Engineers, Vicksburg District, on three field research projects involving the water quality sensors mentioned, and we are currently planning a fourth. We see interagency cooperation as necessary to achieve the concentration of effort and funds needed to provide a workable solution to the sensor problem. Interagency cooperation would also tend to reduce duplication of effort.

The following persons were interviewed for this report and their cooperation is acknowledged.

Mr. Paul Duffy - U.S. Forest Service, Oxford, MS
Mr. John Burt - Soil Conservation Service, Fort Worth, TX
Dr. Ronald Menzel - SEA, Durant, OK
Mr. Gary Miller - SEA, Durant, OK
Dr. Ken Renard - SEA, Tucson, AZ
Dr. Don Chery - SEA, Athens, GA
Dr. Jim Rhoades - SEA, Riverside, CA
Dr. Jerry Ritchie - SEA, NPS, Beltsville, MD
Dr. John Schreiber - SEA, Oxford, MS

FEDERAL, STATE AND LOCAL
WATER QUALITY MONITORING NEEDS

As one of the primary water quality measurement needs deals with environmental quality, and this need spreads across state and local agencies as well as Federal programs, representatives of two EPA Regional offices were invited to present a discussion of these needs at the Workshop. As time would not allow such presentations by each of 10 EPA Regional offices or several representative states, it was felt representatives from two Regional offices having particularly active interests in automated sensor applications would best provide the overview desired. Through their implementation of environmental water quality standards and regulations, EPA Regional offices have an intensive working relationship with state and local environmental and other agencies interested in water quality, and therefore have the opportunity of being aware of the integrated, complex needs of these various groups.

A narrative statement addressing this matter was prepared by Mr. Clifford Risley of the EPA Region V office in Chicago and Mr. Leonard Mangiaracina of the Region III office in Philadelphia. That narrative is presented on the following pages. Mr. Risley summarized these remarks in a 20-minute oral presentation to the Workshop.

FEDERAL, STATE AND LOCAL WATER QUALITY MONITORING NEEDS: AN EPA REGIONAL VIEWPOINT

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Our message today can be stated briefly. The reduction of the pollution of our environment is a tremendous challenge which requires an effort at all levels of government and business enterprises. It affects nearly everyone and, as a consequence, is of interest to most of our concerned citizens.

Pollution control has been the subject of much legislation and a large expenditure of legal and technical effort. It has resulted in the investment of billions of dollars by private enterprise and by government. Ultimately, to make the whole system effective, we will have to monitor the results of our pollution control efforts. Maintenance of high water quality standards, thorough and equitable enforcement measures, and protection of public health mandate a complete surveillance program.

We do not have the manpower to monitor pollution control in an effective manner, nor can we afford the investment in manpower necessary to do the monitoring effort using the traditional techniques of collecting samples by hand and taking the samples to the laboratory for analysis. We also cannot afford to wait days for the analysis, data interpretation and reporting before taking action. This is true whether we are talking about control of the waste treatment process and subsequent discharge; or of the local, state, and national agencies' ability to monitor and take action to prevent pollution or to take prompt enforcement action against violators.

The only way we can provide environmental monitoring in a manner which is sufficiently thorough and rapid enough to give us effective pollution control will be through the use of advanced technology systems. We must utilize automated monitoring coupled with a computerized evaluation and alerting system. This will ultimately be greatly enhanced by integration with remote sensing and rapid communication networks.

Most of the technology needed to do this job effectively has already been developed and such systems are in use in some locations. We have the automated monitoring packaging technology, we have the computer technology, we have the analytical technology, we have the remote sensing technology and we have the communication technology.

Our weakness is in sensor technology which at this time limits the potential of the rest of the system.

I firmly believe that we will get a commitment to invest in these advanced systems by Federal, State and local government, and by industry, when they are convinced that the complete system exists. Ultimately, they must make this investment because they will not be able to ignore their monitoring responsibility and they will not be able to afford the large expenditure necessary to carry out the monitoring responsibility by less efficient manual methods.

Now, I want to go back and elaborate on the points which I have just outlined. I particularly want to emphasize the monitoring needs and attendant sensor needs at local, state and national levels.

The Pollution Control Challenge

In December of 1970, just seven years ago, the United States officially declared war on pollution by establishing the Environmental Protection Agency (EPA). Since then Congress has appropriated billions of dollars to wage this war. It has invested in the building of municipal waste treatment facilities, in supporting state and local agencies, in legal action and in research and development. But over the past seven years, EPA has learned that an essential element for waging a successful campaign against pollution is missing. That element is an adequate knowledge of the enemy, its whereabouts, its source, its concentrations, its characteristics, and its effects.

Maintenance of high water quality standards cannot be assured unless there is a stringent operating program with constant surveillance of river conditions and means to provide quick and appropriate ameliorative action. Even the most skilled and experienced engineer or scientist cannot determine the quality of water just by observing it or from a few grab samples.

The common practice of the past and present is to send people out to pick up samples for later analysis in a laboratory. In order to conduct an effective monitoring program, EPA must turn to sophisticated intelligence gathering techniques such as remote sensing and automated monitoring. While remote sensing and automated monitoring are not expected to totally replace the traditional manual sampling and laboratory pollution analysis, they can provide a speed, perspective and mobility that can be obtained in no other way.

All the latest scientific aids must be utilized to prevent pollution. Effective and economically feasible measures and methods to improve water quality can be achieved only by better collection of pollution data, using automatic water monitoring techniques across the waterway system involved. Processing data in the form required by engineers and scientists, as the basis for sound planning and action, is a necessary part of this operation.

Trend Information

"Accurate and timely information on status and trends in the environment is necessary to shape sound public policy and to implement environmental quality programs efficiently." This statement from the third annual report of the Council on Environmental Quality underlines the fundamental need for the Environmental Protection Agency (EPA) to acquire pertinent environmental data.

Environmental quality data have been collected on a nationwide basis for a number of years but the ability to discern trends on a national or even a regional scale is lacking. Further aggravating this situation is the fact that the list of mandated and suspected pollutants requiring surveillance is growing.

Monitoring Expenditures

EPA currently spends approximately $33 million annually on environmental monitoring. State and local pollution control agencies spend approximately twice that amount. The private sector is estimated to spend in the order of $50 million to $100 million annually on source monitoring. Even at these levels of expenditure, monitoring coverage, both spatially and temporally, is extremely sparse because of the relatively high costs of monitoring. With the current state of the art, monitoring expenditures will have to be increased severalfold in order to provide essential data on standards violations, emerging problems, and overall successes or failures of pollution abatement efforts. Because of the magnitude of these expenditures, effort toward improving monitoring efficiencies is warranted. In that monitoring is an iterative process generally to be continued indefinitely, any improvement in the efficiency of monitoring systems will represent cumulative savings that are realized from that point forward. Accordingly, even at the current level of activity, a one time increase of only five percent in monitoring efficiencies will result in an annual saving to the public sector of approximately $7.5 million.

Considerable effort has been expended by the National Aeronautics and Space Administration (NASA), the Department of Defense (DOD), and other governmental agencies, and a number of private organizations in the development of remote sensing systems for deployment in satellites, in aircraft, and on the ground to observe and record certain conditions and characteristics in the biosphere. Sufficient work has already been done inside and outside EPA to demonstrate the feasibility of utilizing certain of these remote sensing techniques, when complemented by in situ measurement and associated data processing systems, to meet some environmental information needs of EPA and state pollution control agencies. In addition, several of these advanced techniques appear to have a good potential, with some adaptation, for meeting a number of other environmental data needs of EPA in more effective and efficient manner than the approaches now employed.

In particular, automated monitoring station networks coupled with data processing and situation centers would have direct application to EPA and State regulatory agency needs.

The Need for Monitoring

The basic items common to any water quality monitoring program include: 1. program design, 2. flow measurement, 3. in situ determinations, 4. sampling, 5. laboratory analysis, 6. quality control, 7. data management, interpretation and reporting.

In considering the water quality monitoring efforts of the federal, state, and provincial governments in both the deep-water and near-shore monitoring and surveillance programs in the Great Lakes, the agencies have concluded that insufficient resources are committed to permit consistent and meaningful progress in achieving water quality objectives.

Significant variations occur in the monitoring effort, coverage, methods of sampling, analysis and reporting of data, parameter selection, spatial coverage, and sample type. Among the things not adequately assessed are the contributions from erosion and rural and agricultural runoff. We have a great need for obtaining a uniform and consistent data base for future descriptions of waste loadings, changes in land usage, and changes in water quality to facilitate comparisons and measures of progress.

Other Regions in EPA and many State Agencies have drawn similar conclusions regarding monitoring in the major rivers, lakes and the ocean.

When you examine the total effort in man years presently being applied to the monitoring effort by all the agencies concerned, it appears to be a sizeable effort, but when you compare this effort with the total manpower requirements needed to accomplish the goals of the legislation it becomes over-whelming; beyond our most optimistic anticipated manpower resources for many years to come.

The best way to extend this effort and to accomplish our objectives will be approaching the problem from a new vantage point. We need to develop new techniques which depend on reliable sensors, automated analytical methods, automated sampling and remote sensing.

Anticipating environmental problems depends on the ability to identify and measure substances in the environment and to observe their trends and effects through well designed monitoring programs. Our present knowledge of the substances within the environment is extremely limited and what we do know has been gained through application of measurement techniques in limited studies and from results accumulated over many years. These techniques have identified hundreds of substances, many of which are toxic or potentially toxic. However, the number of unidentified substances continues to increase each year as more synthetic substances enter the environment from more sources, from the manufacture, use, and disposal of new commercial products and from emerging energy technologies. Effective identification and control of these pollutants will require more monitoring than we have been able to provide. We need better instrumentation, techniques, and quality assurance procedures for accurately describing and evaluating the origin, vectors, and effects on both human health and the environment.

State and Federal Monitoring Requirements

State and Federal Agency requirements for water quality monitoring are similar. They are shared in many instances, but the response time requirements are different. The state should respond rapidly to municipal or industrial waste treatment plant failures, bypasses of wastes, accidental spills from storage areas, transportation accidents, or acts of nature. The state needs to assess the hazard and protect the affected population, whether they be in immediate contact with the incident or are users of the water downstream. Federal agencies are called in when interstate water bodies are affected or upon request by the state agencies.

Historically, regulatory agencies have been alerted when a sportsman reported a fish kill, a farmer had ill or dying livestock, or a municipality or industry detected a change in odor, taste or appearance of the water supply. They respond by sending out field crews to collect samples.

This is obviously a reactive system which responds only after damage has been extensive. It does not prevent major pollution events nor can it detect them early enough to help minimize the event. In fact, it relies on chance and may miss the event until it is too late to prevent major damage to a downstream water supply.

We cannot hope to prevent major pollution effects unless and until we develop a real time automated monitoring system network which can detect a spill, or discharge violation, evaluate the data, and communicate the information to alert the concerned regulatory agencies with minimum delay.

As we know automated, self-powered in situ water quality sensors have been around for a long time. However, during the last 5-6 years they have undergone extensive development and improvement, especially in terms of the reliability of the sensors, the data control package and readout device. Also, automated field records (cassette tapes) and field data memory units which dump data to satellites or telephone lines are now well developed and used by NOAA, USGS, some EPA Regions and some states.

The major problems with present systems are: the most reliable sensors are T, Cond, DO, pH, but only a few specific ion electrodes. Measurement of salinity by even the new probes is rather weak; the best method is straight conductivity without trying to convert, via electronics, to "salinity". Specific ion electrode development is progressing slowly. The great need is on specific chemical ion probes--our interest is high with regard to ion probes.

Region III favors in situ water quality monitors and the field "dipping" units like Hydrolab and Martek gear.

The big problem is that you need those fixed, in situ devices (like Annapolis Field Office (Region III S&A Div) (AFO) used to have and the states, basin commissions, and U.S. Geological Survey now have) only if you have a full-blown monitoring program.

As of now, there is no Region III dedication to a regional, water quality monitoring program. If we had an estuarine, or river, or region-wide stream program, then we would have need for the fixed in situ monitors.

There are monitoring programs in Region III which use state-of-the-art in situ stream monitors. Examples are: Ohio River Sanitation Commission (ORSANCO), Susquehanna River Basin Commission (SRBC), and Delaware River Basin Commission (DRBC) which all have automatic in situ monitors throughout their respective river basins. Interstate Commission of the Potamas

(INCOPOT) has them, and some states (PA, MD) have their own monitors in state stream/river programs.

The point is that the states and commissions with defined programs already do use monitors in fresh water streams, but we don't know of any monitors used in a major program within estuarine Chesapeake Bay and estuarine rivers or creeks. There are a few isolated personal studies such as Bob Corey's at Smithsonian Institute (SI), one at Virginia Institute of Marine Sciences (VIMS), and one at Chesapeake Bay Institute (John Hopkins) (CBI) which use monitors.

The primary goal of a monitoring program is to provide the information required to identify water quality issues and to assess achievement of water quality objectives. The water quality objectives in this general context include not only those parameters with numerical limits but also the concept of non-degradation of water quality. A secondary goal is to provide the information needed to relate achievement or non-achievement of the objectives to a particular cause. These goals require the measurement of both water quality conditions in space and time and material loadings to the receiving waters. The goals also require or imply a framework in which to analyze the data. The proposed monitoring program, therefore, includes all the elements or components necessary to obtain these general goals.

Concerns for water quality are related to uses which require a specific level of water quality and to uses which adversely affect the water quality. Water must be protected for the most sensitive use. The elements of environmental concern resolve into a series of technical issues which include:

- Enrichment
- Organic contaminants
- Metal contaminants
- Radioactivity
- Suspended materials
- Microbiology
- Dissolved materials
- Trash, flotsam, jetsam
- Thermal inputs

State and Federal regulatory agencies need full-time monitoring for:

- Municipal waste treatment plant effluent permit compliance
- Industrial waste treatment plant effluent permit compliance
- In stream monitoring for water quality trends, to determine loadings, and rural and urban runoff characterization (sediment loadings, nutrient and pesticide contributions)
- Provision of spill alert, storm and combined sewer overflow inputs
- Lake monitoring in areas where potential for spills exist

- Estuary monitoring in areas where potential for spills exist

These agencies need short term intensive monitoring capability (a few days to a few weeks):

- To provide data for enforcement actions and case preparation
- For river, lake and estuary characterization, trends, modeling, and planning corrective actions

They also need emergency response capability. They should be able to move out to the field site rapidly via helicopter or other rapid transportation so that they can define the affected areas and determine the concentrations and seriousness of the situation. They must then take actions to confine the incident as much as possible, alert and protect the public, and take corrective action. Rapid intensive monitoring is still necessary to measure the effectiveness of these corrective actions.

Measurement needs--

Data read-out devices, memory packs, recorders, and power supplies are well developed. We have needs for chemical sensors. We are successful with t, Cond, DO, pH and Reference sensors. We need reliable specific ion electrodes for field as well as for lab use. We would be very interested to be informed on the development of rugged, interference-free field probes for:

- NH_4^+/NH_3
- Cl^-, F^-, Br^-
- CN^-, SCN^-
- CO_2;alkalinity; acidity
- H_2S, HS^- or $S^=$; $SO_4^=$
- NO_3^-, NO_2^-
- ClO_4^-
- redox (fairly well developed)
- Metal species - still open for development and any other inorganic complexes on the shelf or being developed

We know that many of these electrodes are already in use in the laboratory for certain special analyses where the analyst knows the general composition of the sample. The real need is for specific ion electrodes which will work in a common "natural" or "partially polluted" stream/river or estuary of unknown chemical compositions. We need specific ion electrodes which will work equally well in "fresh", estuarine, and marine water--i.e., across the range of ionic strength change due to increase in dissolved halogens.

We would like to know of new methods of interference prevention, electronic "block" or "nulls", strengths and weaknesses of various new sensors. We would expect that NASA's chemical instrumentation and miniaturization, medical science industries advances, and the R&D of companies like Orion, L&N, Beckman could make a workshop very worthwhile and valuable to someone knowledgeable in the field of in situ chemical instrumentation.

If Regional management has a region or Bay-wide field monitoring program we would need this information for maintenance of permanent in situ monitoring stations. Presently, we could use the information for our potential portable in situ monitors (Martek & Hydrolab) and our laboratory specific ion probes.

The operating programs of Region III were contacted to determine their interest and needs relating to Automated In Situ Water Quality Sensors.

The Enforcement Division would like to see a water quality sensor system developed that could be used for the detection and early warning of oil spills in remote locations. Interest was also expressed for the development of water quality sensors that could be used to assist in achieving improved compliance monitoring. This would involve the development of multi-purpose sensors and placing the sensor units at strategic outfall locations.

There were also suggestions that in situ monitoring capability be improved by developing a dissolved oxygen sensor that has greater operational stability, reliability and respectability.

It was also felt that the possibility of developing a technique that would provide the capability of determining subsurface conditions from surface or near surface reading using remote sensing systems should be explored.

The Chesapeake Bay Program is currently undertaking the development of a baywide monitoring strategy that would determine the ambient water quality conditions in the Chesapeake Bay. It would be considered extremely valuable and, in all probability, cost effective to utilize multi-purpose in situ water quality sensors placed in strategic locations throughout the Bay. These should possess the ability to monitor and transmit water quality conditions to a central receiver. This would provide the capability of both recording the quality of the Bay at any point in time and to observe trends in water quality on a close to real time basis.

The need to develop practical in situ water quality sensors is a necessity if extensive and effective water quality monitoring of large water bodies is to be a reality.

Limitations of Manual Sampling

Monitoring has long been undertaken by field sampling and laboratory analysis. The costs are high and the scale of information is restricted. A significant limitation is the time between water becoming suddenly polluted and this event being recognized. Delay in tracing the source and taking corrective action can cause considerable risk to public health and extensive damage to water ecology.

Among the major disadvantages to manual sampling are:

- Manpower is the largest direct cost in a monitoring program.
- Response time to transport men and equipment to the field is extremely long especially where large distances and combinations of air, land, and water travel are involved.
- Time delay between sampling and subsequent laboratory analysis is greater than response time, thus aggravating the situation.
- Time delays can result in significant changes in the quality of the sample.
- Time delay between sampling, analysis and reporting is time lost before taking corrective action.
- Manual sampling is inconsistent, requires considerable operator training and it is difficult to assure quality control over difference in operator technique.
- Manual sample collection is inefficient. The number of stations collected and frequency of collection is limited by distance and number of men in the field.
- The frequent necessity to keep manpower in the field around the clock requires several rotating shifts of manpower. This is very expensive and inefficient.
- Field personnel cannot anticipate when and where spills will occur. They can only respond well after a spill has occurred.
- Field personnel cannot anticipate when infrequent peak discharges from outfalls will occur; must keep around the clock vigilance with the hope that they will catch the peak.
- Significant variations occur in monitoring coverage, methods, analysis, and reporting.
- It is nearly impossible to measure rainfall events, urban runoff or agricultural runoff through manual sampling methods.
- It is nearly impossible to provide any uniform and consistent data sets through manual sampling methods.

The decision whether to sample manually or use automatic monitoring is far from straightforward, and involves many considerations in addition to manpower and equipment costs.

The decision to use automatic sampling equipment does not represent the universal answer to water and wastewater characterization. For initial characterization studies, proper manual sampling may represent the most economical methods of gathering the desired data. It is also prudent from time to time to verify the results of an automatic sampler with manual samples. Also, manual grab samples are often taken during visits to sites where automatic monitors are installed in order to obtain data on certain parameters, e.g., metals, organics, DO, oil and grease, coliform bacteria, etc., that cannot be meaningfully measured from samples taken by automatic equipment. Additional sensors may change the balance of future decisions in this regard.

The use of automatic samplers is indicated where frequent sampling is required at a given site, where long-term compositing is desired, where simultaneous sampling at many sites is necessary, etc. Automatic sampling will often be the method of choice for storm-generated discharge studies; for longer period outfall monitoring, for treatment plant efficiency studies; where 24-hour composite samples are required, and so on.

The assessment of water quality is often based on information and data obtained from surveys, investigations and routine monitoring activities conducted by a large number of institutions for a variety of purposes. The lack of a coordinated monitoring program, including adequate data quality assurance, means that the data are suspected and that long term trends in water quality are difficult to develop. Automated monitoring should be of considerable help in this effort.

Monitoring in Large Municipal Waste Treatment Plants

Automated Monitoring is no stranger to managers and operators of modern waste treatment plants in large cities. Likewise, sensor problems and limitations are well known in these facilities.

Automated Monitoring systems have been used for portions of the waste treatment plant control in some plants for many years, but never extensively. Recent attempts to control most of the treatment process have been attempted by a few plants without complete success.

The primary reason for the paucity of instrumentation used in existing wastewater treatment plants is the unsatisfactory performance of many of the primary measuring elements and analytical sensors. Since most of the measuring elements interface directly with raw sewage, mixed liquor, or thickened sludge, these devices are subject to rapid fouling. Accordingly, they need more frequent cleaning and calibration. Several on-line measuring devices for assessing the organic concentration (TOC, TOD, COD, and respirometry) of wastewater are commercially available at this time. These online analyzers require copious amounts of skilled maintenance, which is usually unavailable in most wastewater treatment plants.

Despite the favorable economics of automatic process control, most wastewater treatment plants use very little automation. A recent survey indicated that automatic chemical addition, residual chlorine control and digester temperature control were used by about 1/3 of the plants.

Virtually all the large facilities utilize central information so that all important events, alarms and treatment information are displayed and recorded in a centralized location. Most new plants used automatic data acquisition systems and approximately 20% of the new facilities use data logging computers. However, only 10% use dissolved oxygen control. Only a few plants have tried to provide central control of a large part of their operation.

Real time computerized supervisory control of large storm and combined sewer networks is in use in several cities. Minneapolis, St. Paul and Detroit are examples of such networks. The vast numbers of variables and control points exceed human computational and decision making capabilities.

Monitoring of the upstream and downstream water quality as a guide to operational control of the municipal wastewater treatment plant was accomplished by Minneapolis, St. Paul. They utilized four water quality monitoring stations to ensure that the city complied with state and Federal Water Quality Standards. They were able to determine from the water quality and flow measurements what degree of treatment was needed. In this way, use of advanced waste treatment techniques was limited to those periods of low flow and low water quality conditions when they were required, rather than to try to operate them on a full time basis or on guesswork.

Monitoring in Small Municipal Waste Treatment Plants

In small municipal wastewater treatment plants, many current rules of operation are based largely on only experience and common sense. Wastewater treatment is a complex, stochastic, dynamic system. A detailed study of its performance requires the use of appropriate techniques that take into account the highly variable nature of relevant inputs such as wastewater flow, strength, chemical composition, weather and outputs such as flow, composition and quality. Some factors have known diurnal and seasonal trends. The practical difficulty in the control of the wastewater treatment plants is that some important factors may not be known; those that are known are not monitored adequately and thus the plant can not be controlled.

There seems to be a tacit agreement between small treatment plants and the states in which they operate that monitoring will not be a topic for discussion. The state asks the plants to monitor their effluent quality to show compliance with effluent standards. Typically, a small plant does not have an operator who can do the laboratory work and its budget is too small to add the necessary personnel and laboratory equipment for extensive testing. The few small plants that do report some effluent quality data, do so infrequently and sometimes the data are unreliable.

Ofttimes a compromise is drawn between a daily monitoring program (which many states want) and no monitoring at all (which small treatment plants want). The compromise is to sample a little. How little is enough to serve both interested parties is never resolved.

Monitoring is not control. It is only the prerequisite for control. Effective monitoring is needed before one knows how much control is required or how effective applied controls have been. The design of an effective monitoring system requires balancing the protection purchased against the cost.

Calculated results from the few available cost studies show that a sampling interval of two or three days should provide protection, yet not overburden a small operation financially. Increasing the penalty for polluting would drive one to more frequent sampling.

If daily sampling is legally required of a small plant, the responsible legislative body is assuming (perhaps without basis) that the cost of monitoring is money well invested. It is, in effect, assuming that the external and public costs of possible occasional pollution exceed the cost of monitoring and control. For small plants receiving industrial wastes which may discharge toxins, and smaller plants in environmental sensitive situations, one might expect the real penalty of being out of control to be great enough to justify not only daily monitoring, but perhaps, even more frequent monitoring (hourly or continuously).

Wastewater flows and concentrations vary constantly. They are influenced by diurnal, weekly and yearly seasonal forces. Sanitary engineers have made few efforts to define these variations quantitatively, fewer efforts to use dynamic models for process design or control, and even fewer attempts to use time series techniques.

One possible reason why time series methods have not been used more often may be because the data base has not existed. Few plants have day to day composite sample analyses. It is rare, indeed, to find frequent grab sampling programs, say, on an hourly or bi-hourly basis.

Monitoring in Industrial Waste Treatment Plants

Many industries have been using monitoring systems for process control. They have developed the sensors necessary to control their process and have been able to do a good job because they can control their flow rates and their inputs of raw materials; and they can conduct either a steady state or controlled batch process. However, when it comes to waste treatment control they have suffered the same problems as the municipal wastewater treatment plant.

The waste flows are intermittent, uncontrolled, variable in quantity, strength and composition and contain a mixture of water, sewage, organic and inorganic process chemicals, oils, toxics and non-toxic substances. Historically, most industries were unconcerned about their waste discharges and only recently have been faced with the necessity to know what is in their waste, how to treat it and how to control their discharge. They, too are faced with lack of good sensors, good automated monitoring systems and know how.

Some material plants have a distinct advantage over the municipal plant in that they do have expertise on hand familiar with automated control systems and sensor operations and maintenance. These plants will have the capability to extend their existing control systems to include the wastewater monitoring and control functions. However, there is no profit motive in this and they will not do so until the regulatory agency demonstrates that it can detect their effluent permit violations and threaten prompt action. At that time industry will step up its monitoring effort in order to protect itself from regulatory actions, and to provide legal proof that it is providing adequate treatment.

Smaller industrial plants face the same problem as smaller municipal plants. They do not have automated monitoring systems for process and control purposes. Even if they have laboratory facilities and personnel, they may not have the equipment or personnel with sufficient time, interest or pollution control knowledge to solve their problems.

Most industrial plants would be very interested in an automated monitoring package that was complete enough and reliable enough to provide their effluent monitoring requirements. Here again, the availability of such systems is limited by the availability of adequate sensors.

Status of Advanced Technology

Automatic water monitoring by a network of stations is clearly the best approach to providing data on the scale required for improved control planning.

The basic chemical and physical parameters to be measured automatically are fundamentally common to all waterways. However, technological difficulties have, until now, restricted the development of satisfactory automatic water monitoring stations capable of operating efficiently within a network. Scientists and engineers have been forced to accept compromises in their basic requirements for data, and higher costs of operation.

Laboratories have had to continue tedious gathering of routine information, rather than concentrating on specialized investigations and analysis of pollutants requiring techniques as yet too complex for incorporation into automatic monitoring on-site.

Automatic water monitoring stations for continuous measurement are currently in use and have demonstrated capabilities of running unattended for periods of four to five weeks. These stations are located in housing on the shore of water bodies and require power lines and communication lines. Such stations use pumps to deliver the water to sensors and sampling equipment located inside the housing where it is protected from the elements and from vandalism and may be heated in winter.

Such systems currently measure pH, Redox (ORP), Cl, conductivity, dissolved oxygen, temperature, turbidity, level, flow, wind speed, wind direction, ambient temperature and solar radiation. These stations can also provide alarms if predetermined levels are exceeded or if any sensor, pump or other component indicates a malfunction. Provision can also be made to automatically collect a series of samples subsequent to a predetermined level alarm or from telemetered instruction.

Automatic cleaning and automatic calibration of sensors can also be provided in such a system.

Experience with such systems indicates that the costs are still too high, they tend to collect too much irrelevant data and the stations are vulnerable to vandalism and contamination. However, these problems will be overcome with greater use of such systems.

A small, helicopter-borne water-quality monitoring package is being developed by the NASA/EPA using a combination of basic in situ water quality sensors and physical sample collector technology. The package is a lightweight system which can be carried and operated by one person as a passenger in a small helicopter typically available by rental at commercial airports. Real-time measurements are made by suspending the water quality monitoring package with a cable from the hovering helicopter. Designed primarily for use in rapidly assessing hazardous material spills in inland and coastal zone water bodies, the system can survey as many as 20 data stations up to 1.5 kilometers apart in one hour. The system provides several channels of sensor data and allows for the addition of future sensors. The system will also collect samples from selected sites with sample collection on command. An EPA Spill Response Team member can easily transport, deploy, and operate the water quality monitoring package to determine the distribution, movement, and concentration of the spilled material in the water body.

Another Water Quality Monitoring System is being developed by NASA for use by the Environmental Protection Agency (EPA) in lakes, rivers, estuarine, or coastal waters for the purpose of monitoring water quality. This monitoring system will utilize state-of-the-art technology in the areas of sensors, electronics, data storage, and packaging; and shall be capable of deployment and recovery from a small surface craft or from an amphibious or low hovering helicopter. The system shall measure and record the concentrations of major constituents and parameters of water in a selected areas, unattended, for a predetermined period of time. The system consists of a subsurface data buoy, a portable surface base station, a special anchoring mechanism, and a sixteen-cell water sampling device.

The subsurface data buoy is deployed manually and will remain anchored in the area of deployment, at a predetermined height above bottom, until retrieved. Data are collected and stored internally in a nonvolatile electronic memory. Sensors shall be selected prior to deployment and data will be taken on a fully programmable basis. The buoy shall have an acoustic transceiver to transmit stored data to the surface on command and to receive control and command instructions from the surface station.

A minimun of six channels of data will be recorded on a programmable time share basis. Specific data are determined by choice of sensor for each channel prior to deployment.

Sensors

It is readily apparent that the primitive state of present sensor technology is a primary constraint on the application of advanced technology to the management of water resources. Many of the needed parameters cannot now be sensed automatically. High priority must be placed on sensor development because a lack of adequate sensors probably will impede other developments for some time to come. We have not committed sufficient resources to sensor development.

The use of aircraft--both high-flying, and low level--has provided remotely sensed water data that have relevance and reliability. These include measurements of the water content of ice and snow, cropcanopy emittance and other parameters related to subsurface water, the dynamics of surface water flux, and many of the water quality and environmental constituents. Present sampling, monitoring, and laboratory techniques are available and, in most cases, standardized to obtain these measurements. In order to utilize space technology, accurate automated stations which can operate service free over long periods of time need to be developed. Their data output can be relayed by satellite or aircraft without the need for human intervention and thus coverage can be provided for many locations, some of which may be remote and difficult to service.

There are two key areas in which substantial breakthroughs are needed to develop ground sensors compatible with the capabilities of satellite-borne data collection systems. First, present equipment is not rugged enough to survive the severities of weather, vandalism, and environmental contamination for periods of six months to one year. The improvement required is largely an engineering problem and should be attainable. Secondly, present sensors either cannot duplicate the laboratory analysis required for detection of many parameters or they require in-place equipment which impedes navigation or other uses of inland water.

In closing, I want to make a plan for use of imagination in sensor development. It is essential that sensor technology be sensitive to user needs, but it is also important that new capabilities not be forced uselessly into old patterns. Since developers of sensors and water resources experts usually are not expert in each other's field, a continuing dialogue between the two is required. The result can be beneficial to both and may produce new approaches in the management of our nation's water resources.

CANADIAN PROGRAMS

In addition to a review of automated water quality sensor applications, research and needs in the United States, Workshop participants heard a description of Canadian activities in this area by Mr. Kenneth Birch of the Canada Centre for Inland Waters. Prior to the Workshop, communication with various U.S. scientists and administrators produced references to active water quality sensor research and leadership in several Canadian agencies. When Canadian representatives were contacted, they were not only receptive and willing to contribute to the Workshop by sending an individual to attend as a special guest, but were highly supportive of such a gathering. The program description narrative, summarized by Mr. Birch in his oral presentation, is given on the following pages.

CANADIAN PROGRAMS

by Kenneth N. Birch
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It is estimated that Canada has about 15 percent of the world's known freshwater resources. Management of these water resources is shared by the federal government and ten provincial governments. The provinces have jurisdiction over property and civil rights and can legislate on their own local water resource matters. The federal government has jurisdiction in specific areas, including national parks, northern territories and situations where fisheries and navigation matters are concerned or where international and interprovincial agreements are made. The activity of monitoring the quality of these various bodies of water is conducted by both levels of government, primarily in the traditional manner of bottle sampling, followed by analysis in a laboratory. (1) Something in the order of 5 percent of this total monitoring effort makes use of in situ sensors or automated field analyzers.

There are 22 automated river monitoring stations currently operating continuously, year round, in Canada. All of these stations are relatively permanent installations involving significant facilities on each site. The locations are shown on Figure 1, while the details about the site, the equipment and the operating agency are outlined in Table 1. The parameters: temperature, pH, specific conductance and dissolved oxygen are continuously measured from a sample pumped from a single intake, which is generally located off the bottom in mid-channel. The sensors are installed in commercial robot monitor systems housed in trailers or local buildings. Heating systems and buried waters with high suspended load, floating debris and ice cakes can cause problems in the spring. Most rivers have vigorous algal growth in the summer which necessitates more frequent system cleaning. The following paragraphs give a brief outline of the equipment and mission of the various stations. (2)

The Province of Alberta operates a network of six Schneider Model 25 Robot Monitors for general surveillance and spills monitoring. Sites are typically located up and downstream of major centres and industrial plants. Data not recorded locally on stripcharts are also telemetered to Edmonton to a central computer facility where they are merged with air quality and stream flow information.

The Water Quality Branch of the Department of Fisheries and the Environment has operated a Schneider Robot Monitor on the Red River at Emmerson, Manitoba since 1968. Two new Phillips PW9835 monitors have been recently installed at the U.S.-Canada border crossing of the Souris River. These stations are part of the 80D, nutrient and dissolved solids monitoring programs in connection with the International Joint Commission and the U.S. Garrison Diversion. The Emmerson station is located in a local water treatment plant and is serviced by the plant operator. It was recently instrumental in the detection and effective documentation of a short duration, but serious, oxygen depletion problem on the Red River. (3) The Souris River stations are equipped with the Phillips ultrasonic electrode cleaners, the automatic high/low level standardization manifolds, and automatic, refrigerated samplers. These stations are scheduled to have GOES satellite telemetry to Saskatoon operational by summer '78.

The Saint John River System is monitored by a network of six stations operated by the Federal Government in co-operation with the Province of New Brunswick. (4) The network is a key part of the monitoring of the transboundary pollution in tributaries to the Saint John River. The monitoring equipment, made by Automated Environmental Systems, has been extensively reworked by its operators and now gives reliable service. The stations are tied together by a leased telephone line and are polled automatically by a PDP8/L based data acquisition system located in Moncton.

The Province of Ontario operates three Schneider Model 25 Robot Monitors and two NERA-Hydrolab units in support of special harbour studies and more recently, studies of pollution from land runoff (PLUARG) in the Grand River. These sites are less permanent than the previously mentioned stations and are serviced on 5- to 30-day schedules. In addition, they also operate two Plessey MM4, self-contained, submersible monitor packages. Data are used with numerical models, together with stream gauge and recording current meter data. (5)

The operators of these river monitoring stations have learned to overcome most of their monitor apparatus problems. In general the temperature, pH, conductivity and dissolved oxygen sensor performance is satisfactory. Six- to ten-percent data loss with 10- to 12-week service periods is reported on the more established system. There is not yet enough experience with the ultrasonic cleaners in the Phillips system to comment meaningfully on the effectiveness, although satisfactory 1-month unattended service over a year was obtained by the National Research Council experimental station on the Ottawa River.

The universal problem seems to be turbidity sensors. Hach, AES and Schneider models have all been tried at several sites and all were found to drift too quickly to be of present value. Turbidity in itself is not considered to be important enough to increase the service frequency at the stations for this parameter. However, if a sensor could be made which had good low range sensitivity, dynamic range from 1 to 10,000 ppm F, and reliable cleaning mechanisms (handling algal growth, suspended material and oil films), then it would be used in many of the Canadian stations. There are some who believe that useful statistical information, related to factors like nutrient loading, can be found from continuous turbidity measurements.

Another problem area seems to be drifting reference electrodes as used for pH and chloride ion measurements. Some of the solid state combination electrodes have been found to work best in the Saint John's network stations.

Apart from the river monitors, Canadians are also making good use of the new types of portable water quality monitors like the Hydrolab Surveyor - NERA system and the Montedoro Whitney Mark II system. These systems have a surface readout and recording unit with sensor sonde which can be lowered to 100 meters with sensors for temperature, depth, pH, conductance and dissolved oxygen.

Regional biologists and limnologists are finding these instruments very useful for surveying the hundreds of small lakes in their regions which they must characterize. Measurements in profile can be quickly taken and plotted on site, such that adequate surveys of small lakes can be completed in hours. Furthermore, these quick surveys permit selection of water sampling sites where the water will be representative of specific zones within the lakes. The net result is a reduction in the number of samples to be carried back to the analytical lab, and an enhancement of coverage within a shorter time than could be realized without these instruments. Generally, users of this equipment experienced a variety of annoying problems initially until they developed their own procedures of transporting, operating and calibrating and after the manufacturers had corrected assorted faults. Defective power packs and leaking cables and connectors were the frequently reported faults.

The Canada Centre for Inland Waters uses water quality sensors in a variety of special systems put together in support of particular research projects. One system (6) automatically measures dissolved oxygen and temperature profiles in three limno corrals by gradually lowering a YSI oxygen sensor through the centre of each corral in turn. The system includes a motor driven jiggling mechanism to effect the necessary flow past the sensor and allows an atmospheric calibration check. A separate system (7), used for estimating primary production in these limno corrals, measures pCO_2 in the air and the water by an IR absorption instrument equipped with an automated sample standard sequencer and packaged for unattended service on a raft. A commercial turbidity meter (8) employing a transmitted/scatter light ratiometer technique was packaged for an in situ profiling application where it was required to trace large sections of water with high suspended load. Adams (9, 10) used two Datel LPS-16 data logger systems to monitor a special array of sensors (22 thermistors, 4 Hydrolab conductivity, 10 wavelength selective irradiance) mounted on an underwater tower in support of studies on effects of oil spills in Arctic lakes.

When asked to identify needs for new sensors the user community in Canada responded with requests for nutrient monitors which are sensitive and reliable over several weeks. This requirement stems from a need to estimate trends of loadings into rivers and lakes within a timeframe of only 1 or 2 years. There is a high degree of temporal variability in nutrient concentrations and discharge such that conventional grab sampling techniques are questionable for this purpose. Nutrient loadings are also becoming reference items in international treaties on transboundary water movements. It is not clear just what nutrient parameters should be measured for this purpose, but most users would suggest total and orthophosphorus, total nitrogen, nitrate and ammonia. These must be measured over the range 1 to 0.005 ppm as N or P with accuracy on the order of 20 percent of reading at the low end range being acceptable. There have been attempts to use a Technicon CSM-6 to continuously monitor orthophosphorus, ammonia and nitrate at a test site on the Red River in Emmerson. It was found that the equipment needed at least daily standardization and frequent cleaning of the plumbing and colorimeter. The filter systems provided with the equipment would repeatedly clog under the conditions at the site. Nevertheless, with one junior technician assigned to attend to this monitor, a year long record was obtained. The experience demonstrated the high variability in these parameters and the lack of reliable equipment to monitor them.

There are other parameters for which sensors would be required. Total organic carbon or total carbon in the range 5 to 20 ± mg/ was requested from some users, but no one had evaluated the UV types now on the market, or had plans to do so. Sensing devices for hydrocarbons and toxic substances were also requested to aid in detecting spill and special runoff situations.

Much of the research and development work in water quality monitoring is being done in support of laboratory based, analytical technology. There is no agency in Canada with a specific mandate to develop or evaluate sensors for water quality monitoring in general. Nevertheless, there is some activity, satisfying some particular research interests, in the universities, National Research Council and the major water resource centres in Canada.

The Analytical Methods Research Section at CCIW has been active in the development of new types of selective ion electrodes and in applying them in semi-automated systems. Sekerka and Lechner (11) have developed an inexpensive solid state chloride ion-selective electrode based on HgS/Hg_2Cl_2 membrane showing overall better performance characteristics than those based on AgCl membranes. It has a response over the concentration range 1×10^{-1} M to 5×10^{-7} M Cl, an electrical impedance in the 100 ohm range, and a response time in the five second range (at 1×10^{-3} M C). A prototype of this electrode is being evaluated in a robot river station in the St. John Network where it is reported to work well in low chloride ranges. The HgS matrix has been applied (12) to electrodes for other ions including bromide (to 1×10^{-7} M), thiocyanate (to 5×10^{-7} M), cyanide (to 5×10^{-6} M), and iodide (to 1×10^{-7} M). Analytical behaviour in respect to selectivity, sensitivity and response is superior to electrodes based on Ag_2S.

More recently a new zero-current chronopotentiometric technique (13) with ion-selective electrodes has been developed. In principle, it utilizes electrodes and gas-permeable membranes for measurement under non-equilibrium conditions, where the speed of the potential change of the sensing electrode is related to the concentration of the ion of interest in the sample. (This technique is capable of determining a variety of species, assuming that a system of chemical reactions leading primarily to the formation of a gaseous species, which passes through a hydrophobic semipermeable membrane, and reacts with ions of the internal solution of the sensor, produces a change in potential of the ion-selective electrode.) A working laboratory prototype has been built and used to measure CN^-. In operation a sealed sample is treated with a hexamine buffer to pH 5.5 and the sensor electrode is mechanically removed and replaced over the membrane so as to trap about 1 $\mu\ell$ of fresh inner electrolyte. As the gas formed passes through the membrane it reacts with a known initial concentration of $AgNO_3$ at pH 11.5 and produces a changing potential at the silver ion-selective electrode. With a 15-second measuring time, ΔE readings of 10 to 130 mV are obtained for 10 to 100 ppb CN^-respectively. The technique has been applied to SO_3- and is expected to be applied to NH_4+, HCO_3, NO_2-, and F- with detection limits in the order of 10^7 technique, there is hope of being able to make a new family of water quality sensors exploiting its features of solid state electrodes, high selectivity and sensitivity, simple sample pretreatment and potential for neat in situ probe-like packaging.

The need for a relatively inexpensive dissolved oxygen monitor capable of unattended, in situ service for several months has been another area where specific sensor research is being sponsored. Membrane fouling and aging limits the use of available membrane diffusion-limited voltametric cells as sensors for dissolved oxygen over long time periods. Fowler and Oldham (14) have developed a cell that employs a pulsed mode of operation and special signal processing called semi-integration. It works on the principle that oxygen will diffuse through a semipermeable membrane to establish partial pressure equilibrium with a small pocket of internal electrolyte, such that when a cathode in that electrolyte suddenly falls to a potential where oxygen can be reduced, then the pulse of current which flows can be semi-integrated to produce a single, m, directly proportional to the dissolved oxygen partial pressure, a_{O_2}. This can be shown as:

$$m = (nAFK\sqrt{D}) . a_{O_2}$$

where n is number of electrons, A is the area of the cathode, F is the Faraday, K is the reaction rate constant, and D is the coefficient of diffusion in the electrolyte. The current is independent of membrane permeability terms and relatively insensitive to temperature and convection factors. For continuous monitoring of dissolved oxygen, the cell is pulsed for 5 seconds every 15 minutes. Also, because the cell rests open circuit, it is very amenable to applications where arrays of DO sensors are needed. Unfortunately, we have been unable to produce a practical field-usable sensor based on this design, apparently because there is a significant background signal which is difficult to control by the fabrication ideas attempted so far.

In lakes research and surveillance programs there has been an outstanding need for an in situ oxygen sensor which could quickly and accurately measure the oxygen profile in lakes. Present day dissolved oxygen sensors respond too slowly to temperature and oxygen changes for them to be operationally useful in profiling instrument systems. CCIW has a study in progress to design and test a prototype oxygen sensing device capable of at least 0.5 second response to both temperature and oxygen. Essentially this work is following the line of medical researchers who have already demonstrated in vitro millisecond response times in blood by miniature membrane-covered probes.

In 1973 the Instrument R&D Unit at CCIW undertook a project to develop a prototype of a new type of water quality monitoring system based on a "Robot Experimenter" concept first proposed by Birch. (15) The research need addressed was that of getting economical in situ and time-series data for a variety of water quality parameters of importance in lake and river studies.

Since suitable sensors for most of these parameters are not available, it was decided to approach the problem by constructing an underwater robot laboratory and programming it to emulate the analytical procedures by which water quality parameters are usually defined. To implement this approach, a family of submersible apparatus modules (e.g. pumps, valves and electrode packages) was created. The underwater robot sensing head is made up of a number (maximum of 18) of apparatus canisters and two, 20-cm-diameter pressure cases containing electronics held together and serviced by a main frame structure. This sensing head is placed on the lake bottom and is connected to shore by a cable which carries power, data and control-signals. An Interdata 74 minicomputer (8K x 16-bit memory) is sited onshore. Resident software, specifically developed for this system, allows experiment routines to be written in a concise, interactive, interpretive language called REM code. It is arranged so that a central computer or a user at a data terminal can telephone the shore based minicomputer to get a readout of data and status conditions or to modify the experiment routines. The flexibility afforded by the modular apparatus and software control makes this system very useful for developing and field testing new ideas for sensor devices and sampling techniques. A recent configuration (V2) of this system operated last year and measured hourly observations of temperature, pH, chloride ion, conductivity, dissolved oxygen, turbidity and total alkalinity from three intakes fixed by a float line at 0.2, 2 and 7 meters off the bottom at a site 2 km offshore in Lake Ontario. This system configuration is being evaluated for time series monitoring applications related to lake surveillance programs. A sample intake profiling (SIP) subsystem has been built for the underwater station so that samples can be taken for analysis from any point or depth interval and so that readings of temperature, dissolved oxygen and turbidity can be taken in profile.

The continued demand for inexpensive, reliable, unattended, nutrient monitoring capability and the apparent lack of excitement with available continuous (auto-analyzer styled) monitors have prompted the development of a phosphorus monitor based on a micro-batch analyzer concept. The monitor will use a modified form of the familiar ammonium molybdate colorimetric method embodied in specially designed apparatus. It will work under computer control to perform the sample preparation, digestion or hydrolysis, reagent addition, colour development and measurement steps in a sequential, timed order. In concept, it will analyze for several forms of phosphorus, one after the other, with self-standardizing methods and be capable of unattended operation for weeks or about 3,000 data points. The first prototype is being built as a module for the Robot Experimenter system utilizing the computer control, data handling and sample taking facilities that the system provides. The apparatus and techniques developed should be extendable, with the use of modern micro-computers, to other parameters and system configurations.

Dauphinee of the National Research Council has developed a prototype zooplankton counter using a conductance cell designed for towing in seawater. (16) The system uses a D.C. current, tubular conductance cell (3 to 5 mm diameter and 1 to 2 cm long) with evenly spaced ring electrodes. Plankton, being near insulators relative to seawater, produce a characteristic signal which can be distinguished from other spurious signals and which contains information on the size and length of the plankton.

In my opinion the most promising technological improvements are to come from good system analysis and design. This will suggest which water quality factors should be sensed and what equipment configurations and sensor devices would be most appropriate to do that job. I sense that managers are expressing their need for monitoring equipment in terms of their present surveillance programs and are limited by the concepts that went into the legislation that authorizes such programs. For example, the so-called "parameters" are often defined by complex analytical accuracy with that achieved by these methods. I believe there are many instrumental techniques which are sensitive to water quality changes and which could be developed as valuable tools in automated monitoring stations, but their value cannot be fully appreciated as long as they must compare to conventional laboratory practice.

System design at the monitor station level should be questioned. Since only a few millilitres of water are really necessary for any water quality measurement and since only one to six samples per hour are generally adequate to describe variations, then is it really necessary to pump huge volumes of water continuously, suffering the cost of installing, maintaining and operating the engineering works that provide it? This need for major site engineering works can be avoided by miniaturizing the plumbing apparatus and packaging sensors so that the entire monitor can be planted in the stream directly. Furthermore, a stable thermal environment without overheating and freezing conditions is afforded by going underwater.

The Robot Experimenter system, mentioned previously, has demonstrated the feasibility of such a submersible station in concept and in many practical ways as well. Of course there are some new engineering problems to be faced in designing such self-contained underwater stations, but there are many advantages to be exploited as well.

Another point of system design which should be reviewed against other alternatives is the need for continuous monitoring and its corollary, parallel direct readout of each parameter. One attractive alternative is frequent batch sampling with some sequential and parallel analysis. In addition to the energy saving in the pumping operation alone, there are advantages to be gained from the fact that fouling and reagent consumption are generally proportional to sample pumping time. Many presently available and accepted analytical techniques become more practical in batch operation as we hope to demonstrate with the phosphorus monitor project at CCIW. The common practice of having completely independent sensor-electronics for each parameter results in duplication of hardware with no reliability benefit. By reducing the hardware to the smallest complement and by employing common signal conditioning and computer compensation techniques, then it should be possible to reduce the cost per monitor.

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TABLE 1: MAJOR RIVER MONITORING SITES IN CANADA

MAP KEY	WATER BODY	SITE	AGENCY	MONITOR MANUFACTURER
1	North Saskatchewan	Vinca	Alberta	Schneider
2	Bow River	Bowness	Alberta	Schneider
3	Bow River	Calgary	Alberta	Schneider
4	Oldman River		Alberta	Schneider
5	Red Deer River	Drumheller	Alberta	Schneider
6	Wapiti River	Grande Praire	Procter and Gamble	Schneider
7	Qu'Appelle River	Edenwald	Saskatchewan	Schneider
8	Red River	St. Agathe	Federal Water Survey	In house developed
9	Red River	Emmerson	Federal Water Quality Branch	Schneider
10,11, 12	Toronto Harbor	(3 stations)	Ontario	Schneider
13	Ottawa River	Ottawa	Ntl Research Council	Phillips
14	St. John River	Grand Falls Dam	Federal Water Quality Branch	A.E.S.
15	Aroostook River	Tinker Dam	Federal Water Quality Branch	A.E.S.
16	Presquile River	Can/US Border	Federal Water Quality Branch	A.E.S.
17	Meduxnekeag River	Belleville	Federal Water Quality Branch	A.E.S.
18	Kennebecassis River	Apohague	Federal Water Quality Branch	A.E.S.

(Continued)

TABLE 1. (Continued)

MAP KEY	WATER BODY	SITE	AGENCY	MONITOR MANUFACTURER
19	St. John River	Beechwood Dam	Federal Water Quality Branch	A.E.S.
20	St. John River	Mactaquac Dam	Federal Water Quality Branch	A.E.S.*
21	Souris River	Canada/U.S. Border	Federal Water Quality Branch	Phillips
22	Souris River	Canada/U.S. Border	Alberta	Phillips
23	Bow River	Medicine Hat	Alberta	Schneider

* presently decommissioned

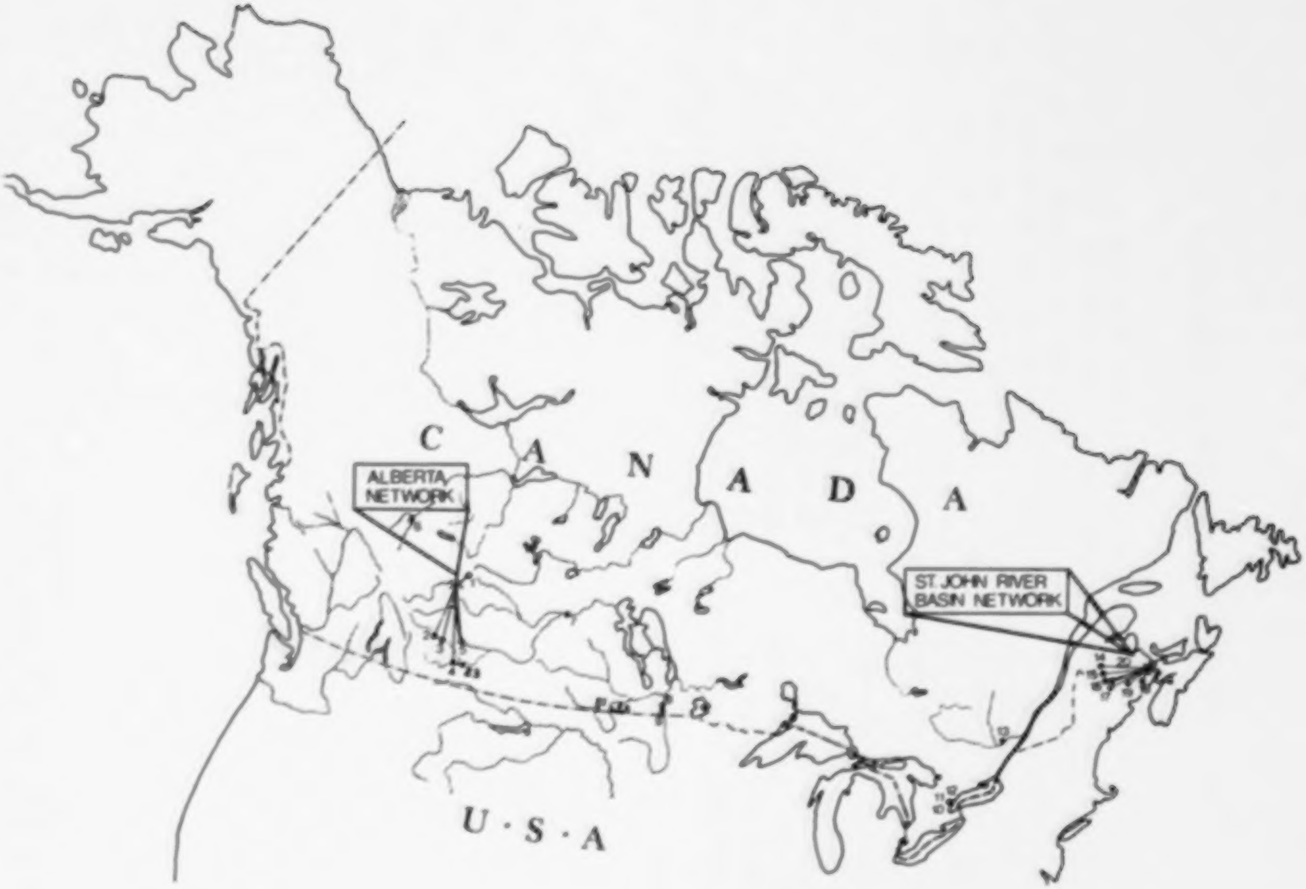
C A N A D A
U·S·A
ALBERTA NETWORK
ST. JOHN RIVER BASIN NETWORK

Figure 1. Major river monitoring sites in Canada

UNIVERSITY RESEARCH PROGRAMS

Representatives of six universities active in water quality sensor research and development were invited to present discussions of their research activities and participate in Workshop work panel discussions. Each was requested to prepare a written narrative for inclusion in this Workshop report, as well as give a 20-minute oral presentation on his topic. The narratives are given on the following pages of this report. The participating university representatives were:

Dr. Roger Bates	University of Florida
Dr. Khalil Mancy	University of Michigan
Dr. Walter Blaedel	University of Wisconsin
Dr. F. H. Middleton	University of Rhode Island
Dr. Richard Newton	Texas A & M University
Dr. Charles Whitehurst	Louisiana State University

RESEARCH ON ELECTROCHEMICAL METHODS FOR ON-SITE DETERMINATION OF TRACE METAL IONS IN NATURAL WATER SYSTEMS: Anodic Stripping Voltametry with Collection

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Madison, Wisconsin 53706

Introduction

On-Site Trace Analysis by Electrochemical Methods--
Electrochemical methods of analysis have great capabilities for on-site monitoring. Almost all such methods involve the application and measurement of potentials up to a volt or two, together with the observation of currents that are of the order of microamps. Equipment and techniques for such measurements are basically very compact and simple, and their use need not be confined to the controlled environment of the large, central analytical laboratory.

Equipment and instrumentation that are commercially available and in general use have usually been designed for high stability, high sensitivity, high accuracy, long life, and versatility, and these qualities tend to locate the instruments in our analytical laboratories. Some important requirements for on-site use in the field are simplicity, portability, and economy, and these are not generally compatible with the requirements for laboratory instrumentation. To adapt existing or conventional equipment and methods to on-site use therefore often requires a compromise, in which some desirable characteristics are relinquished or achieved by other means, in favor of characteristics that are desirable for on-site use. The on-site application of anodic stripping voltametry (ASV) may be achieved by such compromise.

In principle, electrochemical methods of analysis are highly sensitive. The potential at an electrode in a chemical system is generated at the electrode surface--it is an interfacial phenomenon--and to affect that potential, only a monolayer of electroactive material may be needed for a potentiometric measurement. An amperometric or coulometric measurement can usually be made easily with the consumption of 10^{-9} coulombs (one nanoamp flowing for one second), which corresponds to 10^{-14} equivalents transformed, and which approaches the femtomole level of detection. In any case, the parts-per-billion (ppb) levels encountered in environmental analysis appear to be well within the reach of electrochemical methods. For some elements, the sensitivity of electrochemical methods exceeds the sensitivities of the more popular atomic absorption methods. Even the sensitivity of activation analysis for some elements may be exceeded by electrochemical methods.

In describing the appropriateness of electrochemical methods for the measurement of ppb concentration levels, it is important to avoid the impression that these levels are easy to measure. On the contrary, the measurement of ppb concentrations has been likened to trying to measure the golf ball concentration of a golf ball in Lake Mead. While this comparison is not accurate, it does point up a very important consideration in low concentration measurements: getting the material to the sensor surface. While sensor quality and sensitivity are necessary, they are not sufficient. For example, installation of the best and most sensitive golf ball detector in the world at the north end of Lake Mead would be of little avail if the golf ball is located near the south end of Lake Mead. Or, a bucket-dipping type of sampling operation would result in a lot of samples with zero golf balls per bucket. (In fact, if a lucky bucket sample were obtained with the golf ball in it, that result would probably be rejected on statistical grounds for being out of line with other replicate samples!)

The message in these remarks is that, in trace analysis, the operations of sampling, enrichment, and separations are intimately bound up with the sensing step, and may require more effort than the sensing step. This is particularly true for electrochemical measurements, which are not highly selective. A main goal of on-site methods is to reduce the sampling effort, and to eliminate the effort, delays, and errors associated with the storage and processing there before the sensor measurement is made.

Anodic Stripping Voltametry (ASV)--

In ASV, the trace metal ions in a water sample are deposited on an electrode held cathodically for a period of time under controlled conditions. After a sufficient amount has been deposited, the electrode potential is scanned in the anodic direction. The trace metals are oxidized, beginning with the most active, giving current peaks whose location on the voltage scale characterizes the metal ion, and whose peak height is proportional to the concentration of the metal ion in the original sample solution. ASV is applicable to 10-20 elements at the ppb level--ones which can be electrodeposited. The elements of particular interest are Cu, Pb, Cd and Zn.

Like any sensitive method, ASV suffers some shortcomings. A principal disadvantage is encountered in the stripping process, as the electrode is being made anodic. This is accompanied by a large current, called the charging current, which gives a high and variable background, and which tends to obscure the smaller stripping currents. The electrode material is mercury, usually in the form of a hanging drop. Mercury is used because of its high overvoltage for hydrogen liberation, which interferes with the deposition of active metals like zinc at other electrode materials.

Anodic Stripping Voltametry with Collection (ASVWC) (1,2)

Summary Description of ASVWC--

ASVWC is a modification of ASV designed to eliminate charging current. Equipment is schematized in Figure 1, which represents a tubular channel through which the sample solution is passed. Two tubular electrodes separated by a small gap are located on the inside of the channel. For the deposition of the trace metals, the upstream electrode (lower electrode in Figure 1) is made cathodic, and the sample is passed through for a controlled length of time (1-10 minutes). The downstream electrode is kept anodic during the sample deposition, to prevent the accumulation of plated materials. For the stripping step, a cathodic potential is applied to the downstream electrode, and the upstream electrode potential is increased linearly with time. As the metals are stripped from the upstream electrode, they are carried by the flowing solution to the downstream electrode, where they are deposited, giving a peak in the plating current. With properly controlled conditions, the peak height of the plating current is proportional to the concentration of the trace metal in the original sample.

Equipment--

The electrodes are housed in an assembly of two Plexiglas blocks (Figure 2), held together with bolts (not shown). The lower block contains a cavity with two 1-mm thick glassy carbon plates separated by a Teflon sheet spacer (0.010" thick) epoxied into the bottom. The solution channel (2 mm dia.) is formed by drilling the assembly to give the tubular electrode configuration depicted in Figure 1. The upper Plexiglas block contains a silver-silver chloride reference electrode wound around a post in the cavity. Bridging between the tubular and reference electrodes is achieved through a glass frit washer or stack of ion exchange membrane washers, sandwiched between the end of the post in the upper block and the floor of the cavity in the lower block.

Samples are introduced from a covered beaker, and air is removed by sparging with a stream of nitrogen. Flow of solutions through the cell is measured with a rotameter on the effluent end, with flowrate control achieved by regulation of the head of solution. The reference electrode compartment is flushed with 0.1 $\underline{M}$ KCl (0.3 ml/min), to prevent accumulation of contamination by slow leakage of sample solution through the bridge.

Startup includes electrodeposition of a mercury film onto the glassy carbon electrodes, which lasts for many determinations. Shutdown includes stripping of the mercury film and scrubbing the tubular electrodes with a pipe cleaner and detergent solution.

Characteristics of the System--

In systems of small dimensions, hydrodynamic regimes are highly stable and reproducible, and many are mathematically describable. For ASVWC with tubular geometry, the dependence of peak collection current (i_{pc}) on the operating and system parameters is theoretically derivable:

$$i_{pc} = 2.023\ N\ \frac{(nF)^2}{RT}\ vD^{2/3}V_f^{1/3}\ X^{2/3}\ C\ T$$

N is the collection efficiency at the downstream electrode, v is the anodic voltage scanning rate at the upstream electrode, D and C are the diffusion coefficient and bulk concentration of the electroactive analyte, V_f is the volume flow rate of solution, X is the tubular electrode length, and T is the deposition time. Some of the dependences have been verified experimentally. For example, Figure 3 is a log-log plot showing the cube-root dependence of the peak collection current on flow rate.

Applications--

Figures 4 and 5 represent ASVWC analyses on synthetic solutions prepared from triply distilled water and reagent grade chemicals. Figure 4 shows the dependence of peak stripping and collection currents on stripping potential for ppb levels of Cu, Pb and Cd. The advantage of measuring collection currents instead of the conventional stripping currents is shown clearly. For example, the collection current peak for copper is easily perceptible and measurable, but the corresponding stripping current peak is not even perceptible. Figure 5 shows the collection current peaks given by 0.02 ppb of Cd and 0.10 ppb of Pb.

Table 1 shows results for the analysis of copper in the city of Madison tapwater by several methods. Study of the table indicates that ASVWC results do not represent the total copper content as determined by atomic absorption. This is ascribed as soluble complexes and colloidal particulates (3). Further examination of Table 1 also indicates that the ASVWC results do not represent the copper ion activity as determined with the copper ion-selective electrode, or by an ion exchange procedure that is presently under development (4). Apparently, many of the complexed or bound forms of copper that do not contribute to the cupric ion activity are electrodepositable and do contribute to the ASVWC copper content. These findings are not at variance with those of other workers who have investigated ASV.

TABLE 1. COPPER IN TAP WATER

Method	Copper Ion Concentration, μmol
ASVWC	
pH 7.1	160
pH 5.0	132
Copper ISE	
pH 7.1	2 (activity)
pH 5.7	80 (activity)
Ion exchange	
pH 7.1	2 (activity)
pH 5.7	58 (activity)
Atomic absorption	240 (total)

Conclusions

Apparatus and techniques are described for ASVWC that appear to have the capability for on-site determination of Zn, Cd, Pb, and Cu in natural waters. On-site capability has been achieved by the following modifications of conventional instrumentation and equipment: (1) use of a mercury-coated tubular glassy carbon electrode instead of conventional hanging drop mercury electrodes or rotated ring-disk electrodes; (2) replacement of versatile commercial polarographic instrumentation with simple battery-operated solid-state circuitry for the application of potentials and the measurement of currents; (3) use of a small battery operated recorder for the recording of currents instead of conventional high-precision line-operated laboratory instruments.

Adaptation of laboratory-type equipment for ASVWC has been realized by relatively simple modifications and compromises that are within the expertise of the analytical chemist. However, automation of ASVWC requires duplication of the manipulations of the operator who performs the analysis. Such manipulation involves not only operation of the equipment and instrumentation, including startup and shutdown, but also selection of the sample and its transport through the various stages of the analysis. The automation is largely a research problem in mechanical engineering. If unattended operation over a long period of time is required, the automation effort will be difficult, time-consuming, and expensive. These disadvantages should be weighed against the disadvantages of on-site use by an operator, or against the disadvantages of only partial automation.

Acknowledgement

This work was supported in part by the Environmental Protection Agency (Grant No. 804179-02-1) and by the National Science Foundation (Grant No. CHE-7615128).

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List of Illustrations

Figure 1. Electrode configuration for ASV.

Figure 2. Twin tubular electrode cell for ASVWC.
(A) O-ring; (B) Cation exchange membranes; (C) Lead to upstream stripping electrode; (D) Cast epoxy; (E) Sample solution inlet; (F) Teflon spacer; (G) Lead to downstream collection electrode; (H) 0.1 M KCl inlet; (J) Lead to reference electrodes (SSCE's); (K) Sample solution outlet; (L) 0.1 M KCl outlet.

Figure 3. Dependence of peak stripping current flow rate.
0.1 μM lead in 0.1 M HCl. One minute deposition time. 1 V/min.

Figure 4. Stripping and collection peaks for 6 nM Cd, 7 nM Pb, and 6 nM Cu in 0.04 M acetate buffer.
5-min deposition time. 1 V/min. Collection electrode voltage, -0.80 v.

Figure 5. Collection peaks for 0.017 ppb Cd and 0.10 ppb Pb in 0.01 M acetate buffer.
12-min deposition time. 1 V/min. Collection electrode voltage, -0.80 V.

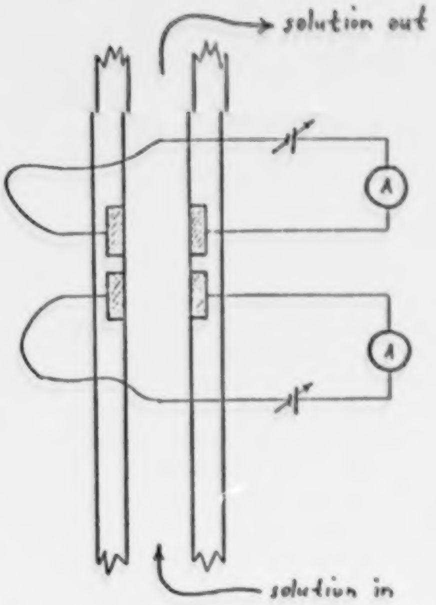
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Figure 1. Electrode configuration

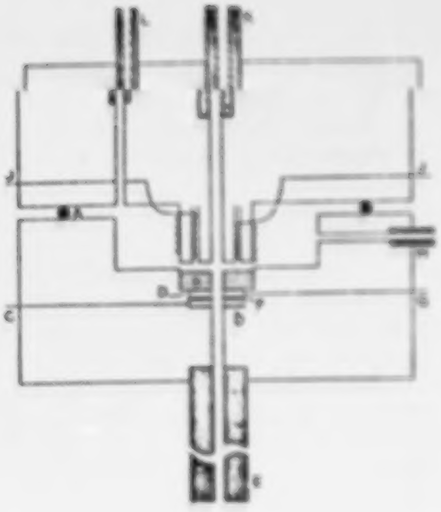

Figure 2. Electrode cell

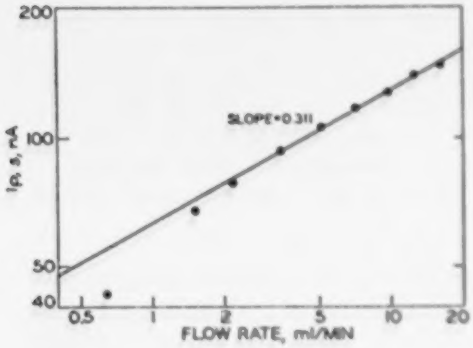

Figure 3. Stripping current dependence

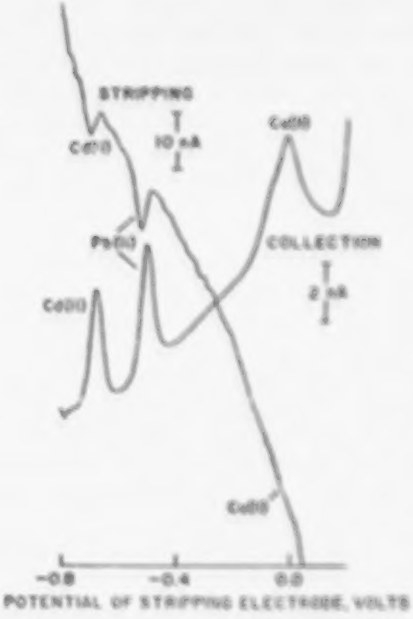

Figure 4. Stripping and collection peaks

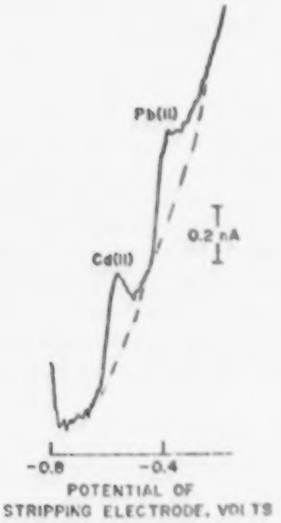

Figure 5. Pb collection peaks

A LIDAR POLARIMETER FOR WATER QUALITY MONITORING

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Introduction

For several years the Remote Sensing Center has been involved in programs for developing methods of measuring water quality parameters. Several devices have been investigated including infrared photography and multispectral scanner systems. Controlled measurements have demonstrated that these techniques have a potential for quantitative measurements of certain water quality factors such as total suspended solids and presence of algae (1), (2). Although worthwhile, these techniques cannot be easily incorporated into in situ measurement devices. In addition, the resulting parameter analysis is generally not real-time.

A new and unique approach to measuring water quality parameters has resulted from the development of an oil spill detection system for the U.S. Coast Guard. The system is a dual polarization laser "radar" termed a lidar polarimeter. It was designed to be located at a fixed position in a harbor area, and scan the harbor as a continuous and automatic oil spill detection system. While the system was not designed as an in situ measuring device, the measurement technique that it utilizes could prove to be useful for in situ water quality measurements. The sensor design also demonstrates present capabilities for automated sensor systems.

The lidar polarimeter oil spill detection system developed by the Remote Sensing Center had to be capable of detecting oil on the surface of water independently of the "background" water turbidity. As a result, it had to be capable of distinguishing between various turbidity levels. It will be shown that the measurement technique employed in this sensor has the capability of continuous, real-time identification and measurement of oil on water and selected water quality parameters including concentration of suspended solids.

Suspended solid particulates are supportive of pollution transport in water due to the adsorptive mechanism. As a result, the concentration of suspended solids can be indicative of pollution potential resulting from precipitation run-off from non-point sources such as timber cut areas, oil shale excavation areas, rangeland, agricultural areas, as well as discharge from industries and municipalities. This is demonstrated by studies (3) that have linked the transport of electrically charged chemicals to suspended clay particles. In addition, sediment and corresponding loads of suspended material in an aquatic system reflect hydrochemical and ecological conditions and their change over long periods of time (4). For all of these reasons sediment and other suspended solids are important parameters in water quality measurements.

Measurement Concept

The measurement technique is to illuminate a water surface with linearly polarized coherent light and measure the light scattered back (backscattered) toward the receiver in both the polarization of transmission (like polarized) and in the polarization orthogonal to the transmit polarization (cross polarized). The interpretation of the backscattered energy is a direct result of theoretical work on electromagnetic scatter by Rouse (5). The development by Rouse indicated that for linearly polarized radiation incident on a surface, the cross polarization back scatter is due to scatter within a volume below the surface. Since the volume scatter that produces the cross polarized backscatter is a multiple scattering process, it is dependent on the concentration of scatterers within the volume.

Recent active optical studies have described the dependence of electromagnetic backscatter upon the subsurface volumetric scattering properties of an aquatic target (6). This work established that the cross polarized backscatter component was almost exclusively dependent upon the number density (turbidity) and size of suspended particles within the medium. These findings led to the development of a laser system transmitting vertically polarized coherent light at 632 nm (red) and receiving both the vertical and horizontal polarized backscatter which provided an accurate measure of suspended solids in natural waterways.

Since most oils act as a lossy dielectric at visible wavelengths, their presence on turbid water can be readily detected as an equal attenuation of both polarization components of the laser backscattered signal. Consequently, reliable detection of oil spills is possible with a single wavelength dual-polarized laser sensor. In addition, the attenuation characteristics of oil vary with wavelength and oil types, therefore the potential exists to actually identify the oil type by employing a multiple wavelength laser system. Further, once the type is known, the thickness of the oil can be inferred from the remote measurement.

As a result of the analysis summarized above, the Remote Sensing Center undertook the development of a prototype dual wavelength system (6) and the single wavelength sensor described herein. The present environmentally hardened sensor employs a 442 nm (blue) laser as the transmitter. The received signal is processed digitally and analyzed in real-time in a small special purpose computer to provide a direct readout of turbidity, presence of oil, the mean and variance of the data and other system flags.

Measurement Results

In order to demonstrate and quantify the utility of a lidar polarimeter to measure water quality parameters and to detect oil, a series of experiments was devised. Controlled laboratory measurements were performed first. These were successful in verifying theoretical calculations and demonstrating the effects of surface roughness, field of view, scatter concentration and adsorbing material. Laboratory measurements were also performed to demonstrate that the presence of oil on turbid water does not affect the depolarization ratio, and that oil type and thickness could be inferred from a dual wavelength system (6).

Measurements were then made under actual field conditions. Measurements made of the Brazos River and the Houston ship channel verified the correlation between depolarization ratio and water quality parameters under actual water conditions (Figure 1-3). These measurements support the use of a lidar polarimeter for remote measurements of turbidity, suspended solids, and transmittance.

The System

The optical head of the 442 nm (blue) lidar polarimeter built for the Coast Guard is composed of three major components: the transmitter, receiver and scanning system. The transmitter is 12 mw Helium Cadmium vertically polarized laser (Liconix Model 401M). The laser is internally modulated with a bandwidth of modulation greater than 100 kHz at 100% depth of modulation. The output of the laser is expanded with a 40x beam collimator to reduce the beam divergence at long ranges and to maintain a safe power density of 2.5 mW/cm^2. The laser transmitter is housed in a 6" diameter PVC tube which is supplied with an externally controlled atmosphere for proper laser cooling.

The backscattered energy from the target is collected with 300-mm f/5.5 telephoto lens. The entire receiver section with associated electronics is housed in a 4" diameter PVC tube located directly above the transmitter. The telephoto lens is mated to an extension tube which houses the spatial and spectral filters along with the recollimating lens. After collimation, the energy is directed through a calcite beam-splitting polarizing tube. The separated vertically and horizontally polarized components are detected utilizing RCA 8645 photomultiplier tubes.

The entire transceiver is mounted on a scanning system which is under the control of a special purpose processor. The scan system is capable of providing 350° arc scan at a rate of

1° per second. The entire system, including the scan system, is constructed of PBC and Lexan capable of withstanding a very harsh environment.

The analog signal processor is composed of four subassemblies, which as a unit are housed aft of the optical system in the receiver column. The system is essentially a dual channel, frequency locked synchronous demodulator, the output of which, after output power normalization, is converted to serial digital data for transmission to the data processor.

The data processor is fabricated around a basic Intel 8080A system with 4K of EPROM and 1K of scratch pad. Within the processor the mean and variance of the data are calculated and a data integration period is automatically selected based on a selected signal-to-noise ratio and system sensitivity. An operating region is established for the selected site and the data are subjected to various filters and tests loops to determine the variance of media turbidity and the presence of oil. Azimuth scan of the instrument is a necessary functional subprogram in the software. Scan speed, direction and current position are monitored and controlled by the CPU. Besides operational functions, the processor maintains system housekeeping for self-test, thermal conditions and status flags.

Outputs from the data processor include an RS-232C standard communications frame which contains all system flags and data along with a buffered alarm signal which is compatible with existing Coast Guard early warning systems.

The operator's console houses the data processor, power supplies for the laser and photomultiplier tubes, the system cooling unit and the operator interface for the selection of functional parameters. The case itself is an environmentally sealed unit which, when closed, maintains a constant atmosphere for the system.

Conclusion

The development of an optical technique of measuring the concentration of suspended solids was described. The unique features of the technique are such that it has the potential of making a quantitative measure of the concentration of suspended solids without many of the difficulties associated with other optical techniques, as well as detecting and qualifying oil on water. The specific sensor discussed herein was designed as a remote sensor and will measure water quality parameters only in the surface layers of water. However, the measurement concept has tremendous potential and could be incorporated in an in situ sensor. Such a sensor could be used to profile water quality parameters in real-time by lowering it through the water medium.

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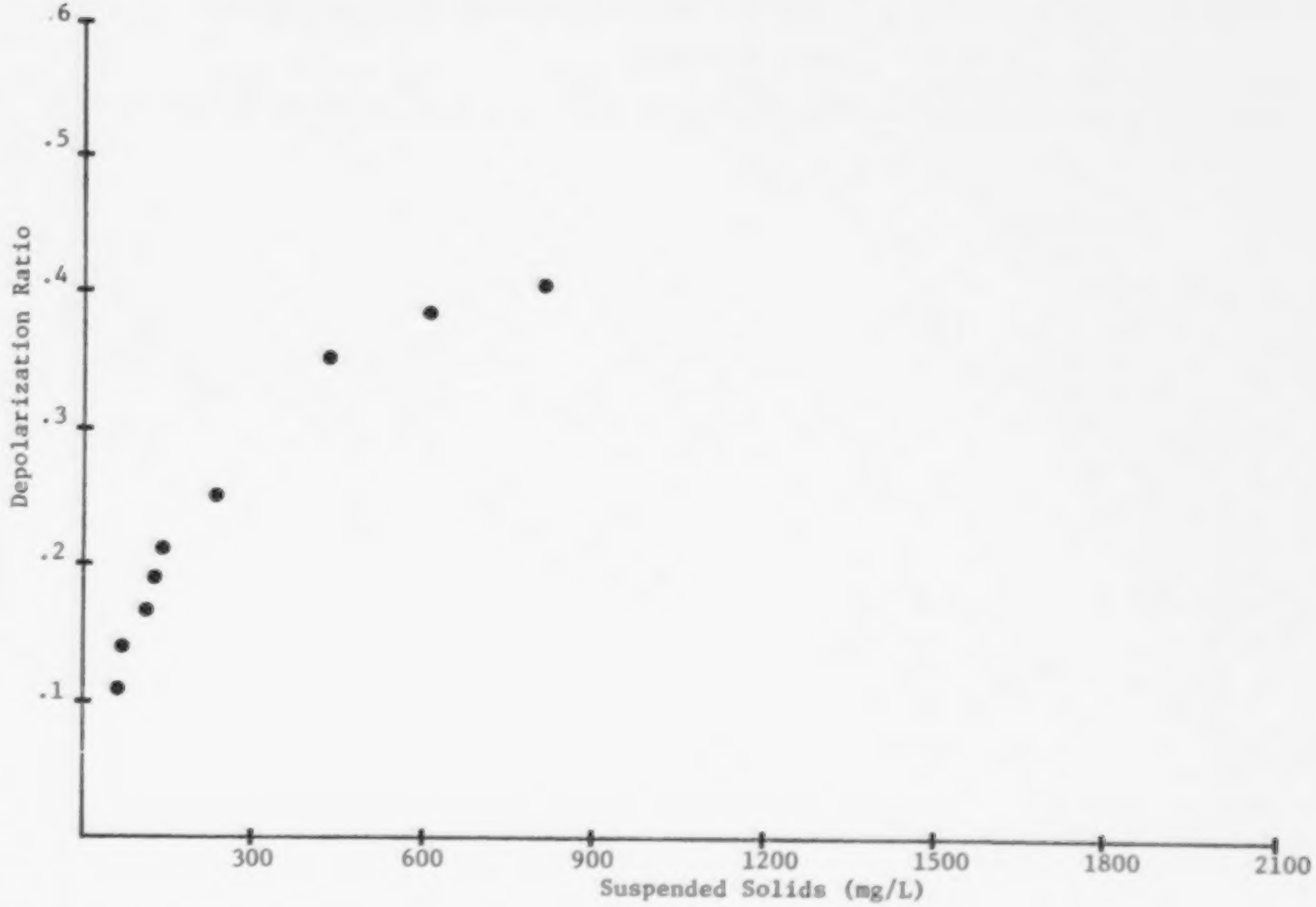

Figure 1. Graph of lidar depolarization ratio as a function of suspended solids observed along the Brazos River from a boat

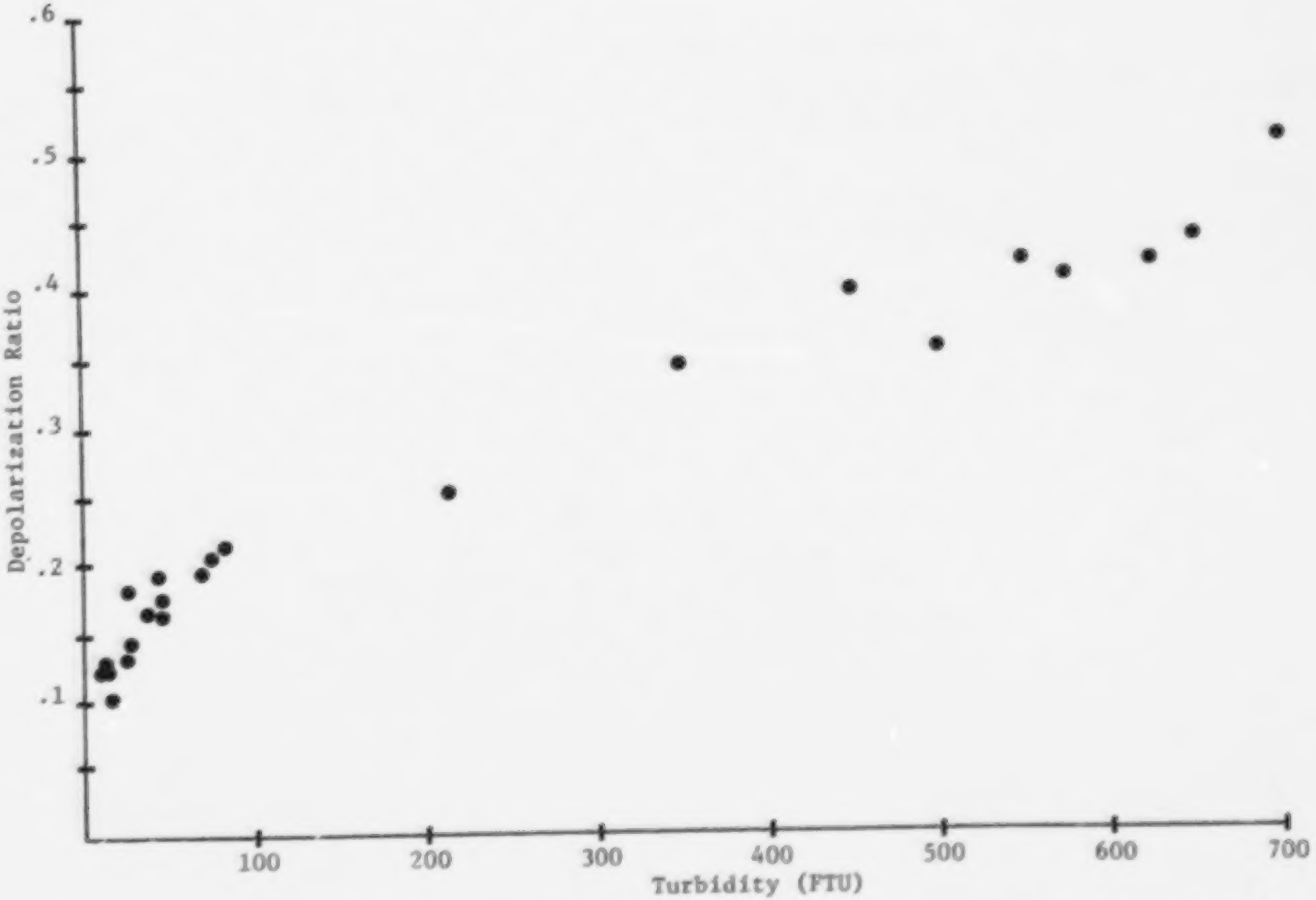

Figure 2. Graph of lidar depolarization ratios as a function of turbidity observed along Brazos River from a boat

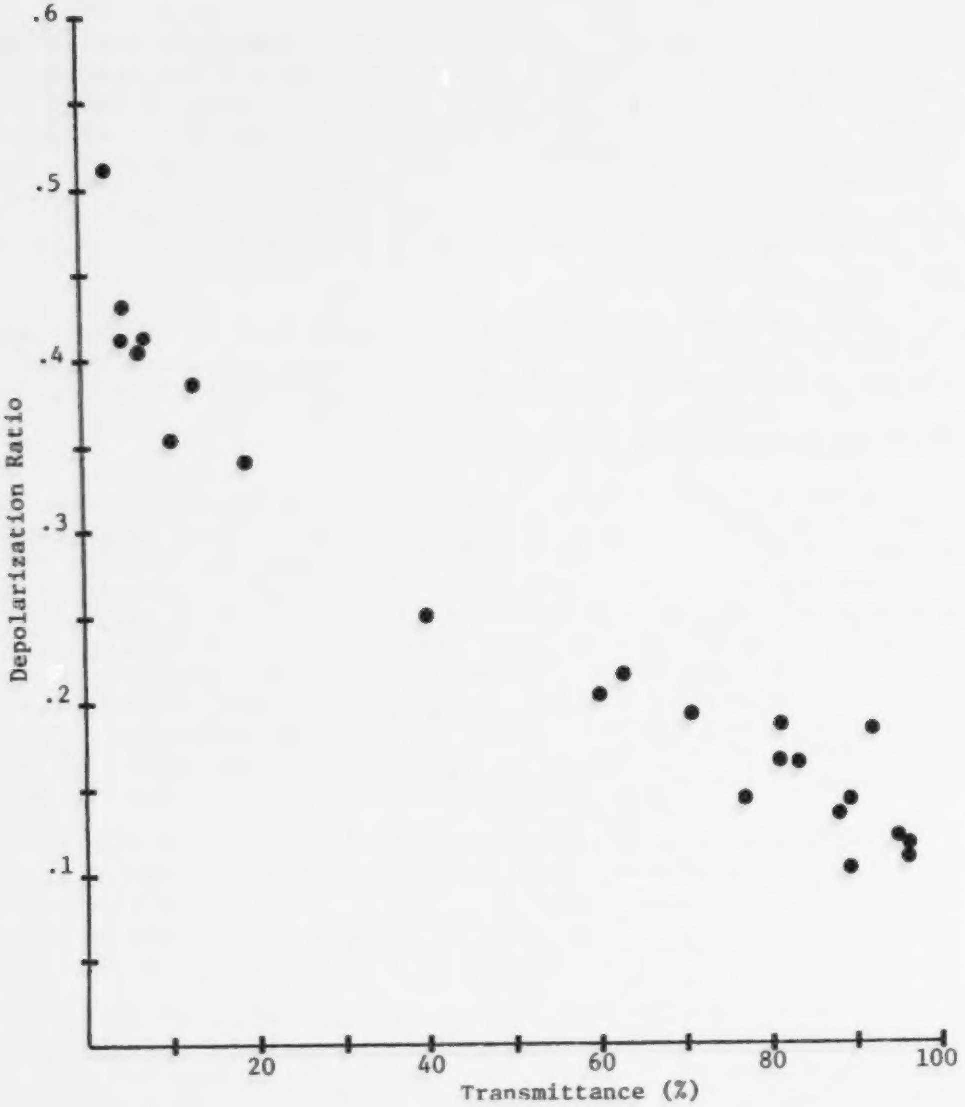

Figure 3. Graph of lidar depolarization ratios as a function of transmittance observed along Brazos River from a boat

NEW WATER QUALITY SENSOR TECHNOLOGY EMPLOYING AUTOMATED WET CHEMICALS

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Among the various water resources research activities at the University of Michigan, there exists an active research program devoted to the development and application of water quality sensor systems. During the last 10 years, this research program has been primarily concerned with the development of new sensor systems and the application of new measurement techniques. This included water quality monitoring and surveillance in lakes (especially the Great Lakes), rivers, and municipal water supplies (1).

This presentation provides an overview of recent research findings, future needs and possible new applications of automated in situ water quality sensors for field application.

In Situ And On-Line Measurement

Water quality surveillance and monitoring programs rely on both field and laboratory measurements. Field measurements are primarily based on either non-contact remote sensing or contact in situ and on-line measurement techniques. Schematic illustrations of in situ and on-line measurement techniques are shown in Figure 1. In this arbitrary classification, the distinction is being made between in situ measurement where the sensor is directly placed in the environment to be measured, and all other field systems offer the unique advantage of the elimination of the sampling step and one needs not to be concerned with the problem of collecting representative samples.

Responses from in situ sensors are proportional to certain physical or chemical characteristics of the aqueous phase, based on established relationships. Typical examples include thermoelectric, photoelectric and electrochemical transducers. Examples of in situ electrochemical sensors are listed in Table 1.

In spite of the distinct advantages offered by in situ measurement, it is frequently more feasible to utilize on-line techniques, which include collecting water samples and bringing them in contacet with the sensor system. This can be done with or without sample pretreatment. The main limitation with in situ measurement is that the sensor response is generally influenced by environmental factors such as temperature, hydrostatic pressure, hydrodynamic characteristics, light intensity, chemical interferences, or nonspecific interferences, e.g., accumulation of oil or grease, silt, or biological growth on the surface of the sensor. The significance of these environmental factors

TABLE 1. ELECTROCHEMICAL SENSORS FOR WATER QUALITY MONITORING

Sensor Type	Equation	
Conductometric	$L = K_C \sum_{i}^{n} C_i \; \lambda_i \quad z_i$	(1)
Potentiometric (2)	$E_m = k + \frac{RT}{zF} \ln \; a_i + K_J a_J^{z_i/z_j}$	
-Glass electrode (e.g., pH)	$pH = -\log a_{H^+}$	(3)
-Membrane electrodes (e.g., ion-selective electrodes)		
- cationic	$pM^+ = -\log a_{M^+}$	(4)
- anionic	$pA^- = -\log a_{A^-}$	(5)

where:

L = specific conductance
K_c = cell constant
C_i = ionic concentration
λ_i = ionic equivalent conductance
z_i = ionic valency
E_m = measured electrode potential
F = Faraday constant
K_j = selectivity coefficient
i_d = diffusion current
A = electrode surface area
P_m = membrane permeability coefficient
b = membrane thickness

depends on the type of the sensor system and the particular application. Automatic compensation for some of these effects, e.g., changes in temperature or hydrostatic pressure, is sometimes possible within certain ranges.

In view of these limitations, it is frequently necessary to conduct on-line monitoring. In certain applications, measurement can be done without sample pretreatment. In other cases, sample preconditioning is necessary (A) to minimize the effect of interferences or (b) for the appropriate use of the sensor system. This may include temperature control, filtration, dissolution, dilution, digestion, or reagent addition. Furthermore, sample preconditioning may be required for the appropriate functioning of the sensor system regardless of the effect of environmental factors. For example, water samples should be adjusted to approximately pH 5.0 prior to the application of the lanthanum fluoride selective ion electrode. This is required to minimize inteferences by hydroxyl ions at high pH or the formation of hydrogen fluoride at low pH values.

In situ and on-line water quality monitoring is frequently conducted by automated systems in mobile laboratories (2), on board ships (3), or by means of remote robot systems situated on shore, or by buoys (4). These are used for water quality monitoring of rivers, lakes, estuaries and marine environments (5). Furthermore, they are frequently applied for monitoring of industrial and municipal effluents and the control of water and wastewater treatment processes (6).

Examples of in situ and on-line water quality sensor systems are given in Table 2. It should be noted that all in situ sensors can be used for on-line measurements, with or without sample pretreatment.

On-Line Measurement With Sample Pretreatment

In view of the previous discussion it is evident that relatively few water quality parameters are presently amenable to in situ measurement or even on-line measurement without sample pretreatment. Such measurements are in general limited to physical parameters and to those chemical constituents for which electrochemical sensors are available. Even in these cases, however, sample pretreatment may be required. For example, since selective ion electrodes measure the activity of a single species (e.g., only S^{--} and not HS or H_2S) it is common practice to account for both the pH and the ionic strength when making specific ion electrode measurements so that the results are directly interpretable in terms of the total analytical concentration. Adjustment of pH is required not only to convert all analyte to the requisite form but also to control the degree of electrode response to H^+ or OH since these ions can, at higher levels, be sensed respectively by cation-and anion-specific ion electrodes.

On-line measurements with sample pretreatment provide extensive possibilities for automated analysis. Examples of such measurements systems are given in Figure 2.

The most common on-line measurement with sample pretreatment is the automated colorimetric analyzer and, in particular, the Technicon AutoAnalyzer system. It should, however, be evident to the reader that the techniques that will be discussed are applicable to many sensors in addition to selective ion electrode and colorimetric analysis. Automated systems have been used in atomic absorption spectrophotometry to present samples to the instrument or to add reagents (such as lanthanum for suppression of phosphate interference), or to perform liquid-liquid extractions prior to measurement (13). Examples of the types of parameters which can be measured by the Technicon AutoAnalyzer are given in Table 2. These are primarily based on automated colorimetric procedures (10).

TABLE 2. TYPICAL APPLICATIONS OF SENSOR SYSTEMS FOR IN-SITU AND ON-LINE AUTOMATED WATER QUALITY MEASUREMENT (PARTIAL LISTING)

---

1 In Situ:

a) Separation and/or concentration:
  - Controlled potential electrodeposition
  - Gas permeable membranes

b) Sensor Systems:
  - Temperature transducers (Thermistors, Thermocouples, etc)
  - Pressure (hydrostatic)
  - Current speed and direction
  - Light intensity
  - Electrical conductance
  - pH-glass electrodes
  - Redox potential-inert metal electrodes
  - Selective ion electrodes (7)
    - Solid state (Free ions)
    - Liquid ion exchange (Free ions)
    - Enzyme electrodes (organic substrates)
    - Gas permeable electrodes (e.g. CO_2, NH_3)
  - Voltametric membrane electrodes (8) (e. g. O_2, HOCl, O_3)

2 On-Line Without Sample Pretreatment:

a) Turbidity
  - Light scatter
  - Light absorption

b) UV absorption (Certain dissolved organic compounds, e.g., phenols). Advanced techniques include compensation for turbidity effects (1).

c) Fish toxicity measurement. Advanced techniques include measurements of both survival and viability (9).

d) All of the above listed in situ sensors can be used for on-line measurements.

TABLE 2. (Continued)

3 On-Line Measurement With Sample Pretreatment:

a) AutoAnalyzers, e.g., Technicon AutoAnalyzer (10).

Parameter	Range(mg/l)	Parameter	Range(mg/l)
Ammonia	0-10	Cyanide	0-3
Nitrate+Nitrite	0-2	Phenol	0-5
Ortho-Phosphate	0-1	Fluoride	0-2
Total Inorganic Phosphate	0-10	Chloride	0-10
Silicate	0-10	Hardness	0-300
Total Soluble Iron	0-10	Sulfate	0-300
Hexavalent Chromium	0-5	Alkalinity (pH 3 min)	0-500
Copper	0-10	Alkalinity (pH 8 min)	0-100
Sucrose	0-100	Total Kjeldahl Nitrogen	0-100
COD	0-500		
Total Phosphorus	0-50		
Detergents			

b) Specialized automated systems:

- Metal analysis by atomic absorption spectrophotometry
- Trace metal analysis by differential pulse polarography or differential pulse anodic stripping voltametry (2)
- Free and total ions using commercially available selective ion electrodes (e.g. Ca^{++}, Mg^{++}, Cd^{++}, Cu^{++}, Pb^{++}, Hg^{++}, S^{--}, F^-, Cl^-, Br^-, I^-, NO_3^-, etc.) (11)
- Dissolved gases or neutral species using voltammetric membrane electrodes (Residual Chlorine-free and total, SO_2, Ozone) (12)
- Total Oxygen Demand (TOD)
- Total Organic Carbon (TOC)
- Calcium Carbonate Deposition Test (CCDT) (2)
- Automated Titrators

A large number of continuous titrators are commercially available. These can be advantageously utilized to both reduce laboratory costs and to improve analysis precision. These devices utilize motor driven, constant delivery speed syringes for titrant addition. Although end points can be sensed, and the titrant addition rate can alter the instrument's derivative circuitry, the analyst should note that this is usually not the limiting factor; the one to which the most concern should be given is the response time of the electrode sensor system. Slow response can lead to over-shooting the end point and thus to an analysis bias.

Automated analysis systems for the monitoring of low concentrations of materials require frequent recalibration. This poses serious limitations to their use in field applications where only weekly maintenance visits to the monitoring station are made. Some presently available equipment utilizes solenoid-activated valves to switch the sample intake from the stream being monitored. Based on the sensor output, the instrument can then be automatically recalibrated from their concentration to that of the sample may not be valid. Dilute solutions often lose strength by adsorption of the material onto the container walls; this can perhaps be prevented by use of inert standard storage vessels such as quartz or Teflon.

Field Applications

Several examples of automated sensor systems are given in Table 2. From this limit it is obvious that there exists a considerable number of possibilities for automated water quality monitoring systems. Depending on the particular use, a given system may not be suitable for field applications. The main limiting factors are usually:

- Ease of operation and maintenance.
- Portability.
- Ruggedness and ability to withstand field conditions with minimum attendance.
- Frequency of calibration and servicing.
- Cost--both capital and running cost.

In a recent study, a number of automated systems were used for monitoring the quality of water supplies in a number of municipalities in the USA (2). This included water quality monitoring at the source, the treatment plant and throughout the distribution system. The purpose of this investigation was to assess water quality deterioration in the distribution system and assess the feasibility of a prototype mobile monitor (a specially equipped van).

A listing of the sensor system used in the prototype monitor is given in Table 3. A summary of the performance characteristics of these sensor systems is shown in Table 4. Examples of automated wet chemical measurements using electrochemical sensors include the use of the lanthanum fluoride selective ion electrode as shown in Figure 3(2), and differential anodic stripping voltametry as shown in Figure 4(2).

TABLE 3. SENSORS IN THE PROTOTYPE MONITOR

Parameter	Sensor Type	Unmodified Commercially Available System	Sample Pre-conditioned	Requires Special Timing Sequence
Temperature	Thermistor	✓		
Conductivity	A-C Conductivity Cell	✓		
pH	Glass Electrode	✓		
Chloride	Solid State Ion Selective Electrode	✓		
Dissolved Oxygen	Voltammetric Electrode	✓		
Free Residual Chlorine	Galvanic Cell	✓	✓	
Total Residual Chlorine	Galvanic Cell	✓	✓	
Turbidity	Nephelometer	✓		
Corrosion Rate	Polarization Admittance Technique	✓		
Free Fluoride	Solid State Ion Selective Electrode		✓	
Total Fluoride	Solid State Ion Selective Electrode		✓	
Alkalinity	Potentionmetric Combination pH Electrode		✓	
Hardness	Liquid Junction Ion Selective Electrode		✓	✓
Nitrate	Liquid Junction Ion Selective Electrode			✓
Cadmium	Differential Anodic Stripping Voltammetry (DASV)		✓	✓
Lead	DASV		✓	✓
Copper	DASV		✓	✓
Calcium Carbonate Deposition Test	Potentiostatic Rotating Ring Disc Electrode			

TABLE 4. PERFORMANCE CHARACTERISTICS OF MOBILE LABORATORY SENSOR SYSTEMS

Parameter	Detection Limit	Range(s)	Selectivity Coefficients or Interferences	Precision	Temperature Dependence	Applicable pH Range	Ionic Strength Effect	Long Term Stability, Recalibration and Maintainance Requirements
Hardness	10 mg/l equiv. $CaCO_3$	One Decade, e.g. 10–100 mg/l equiv. $CaCO_3$	Zn^{2+}=3.5 Mg^{2+}=1.0 Fe^{2+}=3.5 Ba^{2+}=0.94 Cu^{2+}=3.1 Sr^{2+}=0.56 Ni^{2+}=1.35 Na^{+}=0.15 Ca^{2+}=1.0 K^{+}=0.10	±5 mg/l @120–150 mg/l equiv. $CaCO_3$	Considered in calculation of hardness from divalent cation activity measurements	5.5 to 12	Considered in calculation of hardness from divalent cation activity measurements	These liquid junction ion selective electrodes have been shown to have stable potentials which permit continuous use for periods up to seven days without recalibration; however, due to the shape of the electrode tip, twice daily attention is required to insure that bubbles have not formed on the tips. Complete rejuvenation of the probes must be performed every 30 days.
Nitrate	1 mg/l	Two Decades, e.g. 1–100 mg/l	HCO_3^-=0.02 CO_3^{2-}=0.006 Cl^-=0.006	N.D.[1]	Thermistor Compensated	2–12	N.S.[2]	
Chloride	3.0 mg/l	0–240 mg/l	OH^-=0.013	± 2 mg/l	Thermistor Compensated	2–12	N.S.	7 days: No known maintainance
Temperature	N.A.	0–120°F	None	± 0.2°F	N.A.	N.A.	N.A.[3]	7 days: No known maintainance
Conductivity	N.A.	0–1200 0–2400 micro MHOS/cm	None	±5 micro MHO/cm	Thermistor Compensated	5–12	This parameter Measures Changes in ionic strength	7 days: Internal flow channel and electrode surfaces must be cleaned monthly
pH	N.A.	pH2–12	Na^+	± 0.02 units	Thermistor Compensated	2–12	N.S.	7 days: No known maintainance
Dissolved Oxygen	0.1 mg/l	0–12 0–24 mg/l	None	± 0.1 mg/l	Thermistor Compensated	2–12	N.S.	7 days: Electrode must be rejuvenated every 30 days
Free Residual Chlorine	0.01 mg/l	0–1.0 0–2.0 0–3.0 mg/l	None	±0.01 mg/l	Thermistor Compensated	Sample pH adjusted to pH 4.5 by reagent addition	Ionic strength adjusted to constant value by reagent addition	Daily checking of calibrations by comparison with amperometric titration is required. Reagent reservoirs must be refilled every 7 days
Total Residual Chlorine	0.01mg/l							
Turbidity	0.01JTU	0–0.1 0–1.0 0–3.0 0–30 JTU	Air bubbles in sample stream must be removed by a bubble trap	±0.02 JTU	N.A.	N.A.	N.A.	7 days: Periodic cleaning of photocell windows maintains sensitivity. Light fouling of the windows does not effect accuracy within the 7 day calibration period

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TABLE 4. (Continued)

Parameter	Detection Limit	Range(s)	Selectivity Coefficients or Interferences	Precision	Temperature Dependence	Applicable pH Range	Ionic Strength Effect	Long Term Stability, Recalibration and Maintainance Requirements
Free Fluoride	0.1 mg/l	0.1—2.0 mg/l	$OH^- = 0.7 @ [F^-] = 10^{-6}$ to $10^{-4}M$ $OH^- = 0.07 @ [F^-] = 10^{-4}$ to $10^{-3}M$ $OH^- = 0.05 @ [F^-] = 10^{-3}$ to $10^{-2}M$	± 0.02mg/l	+0.17% increase in apparent signal for 1°C increase in temp. (Theoretical)	Sample pH adjusted to pH 5.0 — 5.4	Ionic strength adjusted to constant value by reagent addition	Daily introduction of standards maintains accuracy and demonstrates integrity of the flow system. Electrodes are known to be stable over very long periods of time. Reagent reservoirs must be refilled every ten days
Total Fluoride	0.1 mg/l							
Alkalinity	10mg/l	60mg/l span e.g. 20—30 mg/l equiv. $CaCO_3$	Residual chlorine interferes, but is eliminated by addition of thiosulfate to the sample stream	± 3mg/l equiv. $CaCO_3$	Unknown	N.A.	Ionic strength adjusted to constant value by reagent addition	Reagent reserviors must be refilled every four days. Recalibration must be performed for each new set of reagents
Cadmium	0.001mg/l	0—0.1mg/l	Trace organics can interfere by giving false peaks. Accurate identification of peak potential indicates the presence of interferences	N.D.	N.D.	Sample pH adjusted to pH 3	Ionic strength adjusted to constant value by reagent addition	Standards are analyzed automatically every six hours. DASV electrodes must be replated daily
Lead	0.001mg/l	0—0.1mg/l						
Copper	0.001mg/l	0—0.1mg/l						
CCDT	N.A.	N.A.	Unknown	N.A.	Unknown	Variation in pH results in variation in rate of film deposition	N.A.	Each analysis is discrete. Electrode must be rejuvenated between each run by cleaning with dilute nitric acid
Corrosion	N.A.	10 calibrated ranges from 0—0.1 MPY to 0—1000 MPY (Mils per yr.)	None	± 5% of range	Temperature variation results in change in corrosion rate	Variation in pH results in variation in rate of corrosion	N.A.	No calibration or maintainance requirements. Internal electronic standard demonstrates instrument integrity.

[1] N.D. = not determined; i.e., a specific relationship between the referenced characteristic and the parameter of interest was not determined for the mobile laboratory sensor system.

[2] N.S. = not significant; i.e., variations in ionic strength of tap waters in the U.S. would not produce more than ten percent variation in the apparent activity of the parameter of interest.

[3] N.A. = not applicable; i.e., the referenced characteristic is not related to the parameter of interest.

The operation of automated monitoring systems is best controlled by means of a minicomputer. This is particularly useful in cases where several systems are running simultaneously. An example of such an application was reported by the above mentioned study (2). All sensor systems in the mobile laboratory are controlled by an on-board minicomputer system which includes a Texas Instruments digital computer, Model 960-A; a Texas Instruments Silent 700/300 teleprinter; a combination high speed paper tape reader perforator; and a Computer Products wide range analog-to-digital (A/D) converter, Model RTP7480). The computer contains 16,384 words of semiconductor memory, expandable internally to 32K, and, with the addition of an external chassis, to 64K. An internal timer A16 input/output digital switching board wired for interrupt, and an internal communications register unit (CRU) expansion chassis, required for 5 to 20 peripheral connections, are options used with the computer. Seven CRU connections are used in the mobile laboratory.

Within the data sampling cycle, appropriate digital outputs are sent to each measurement system (a total of 18). Independent programs, operating from the internal timer in the computer, send digital output signals to each of the measurement systems.

In the data sampling cycle, the internal interval timer controls the timing for reading the analog signals from each of the different sensor instrumentation packages. The data acquisition program in the computer determines the gain to be used in the analog-to-digital converter (ADC) in reading each analog input channel. Within the computer, all program operations are under the control of the Texas Instruments supervisor program, PAM (Process Automation Monitor).

Recommendations

The recommendations given below are not restricted to automated wet chemical applications.

1. It is recommended that a unified terminology be adopted for sensor performance characteristics. This can be separated into (a) primary performance characteristics including sensitivity, selectivity, detection limits, response time, and long time stability, and (b) secondary performance characteristics including environmental effects such as temperature, hydrostatic pressure, hydrodynamics, light intensity, ionic strength, etc.

2. Future research and development should emphasize both the improvement of existing sensor systems and their adaptation for field applications, and the development of new sensor systems.

3. Research and Development of water quality sensor systems should include the characterization of soluble and insoluble matter, both in the aqueous phase and sediments. Most trace metals in aquatic environments associate with the particulate matter and sediments, including aquatic biota. The soluble fraction of trace metals may be insignificant in certain cases.

4. It is proposed that a better means of utilization of easily measured water quality parameters be examined. This could be done by first establishing correlation coefficients between one or more easily measured parameters and those parameters which cannot be easily measured. It is important to note that these correlation coeffients will vary from one application to another and could also be time-dependent.

5. Similar to item 4, an easily measured parameter could be used to trigger an automated sampling device and an alarm system. The sample will be then collected for detailed laboratory analyses.

6. It is proposed that the application of in situ separation and concentration techniques be investigated. This could be done for sampling of trace metals or organic matter using electrodeposition or especially designed membranes. Furthermore, in situ separation and concentration could be used in conjunction with voltammetric and selective ion electrodes to provide more effective in situ sensor systems.

7. It is recommended that the application of advanced polarography for trace organic analysis be encouraged. Unfortunately, little emphasis is given to this application in recent literature.

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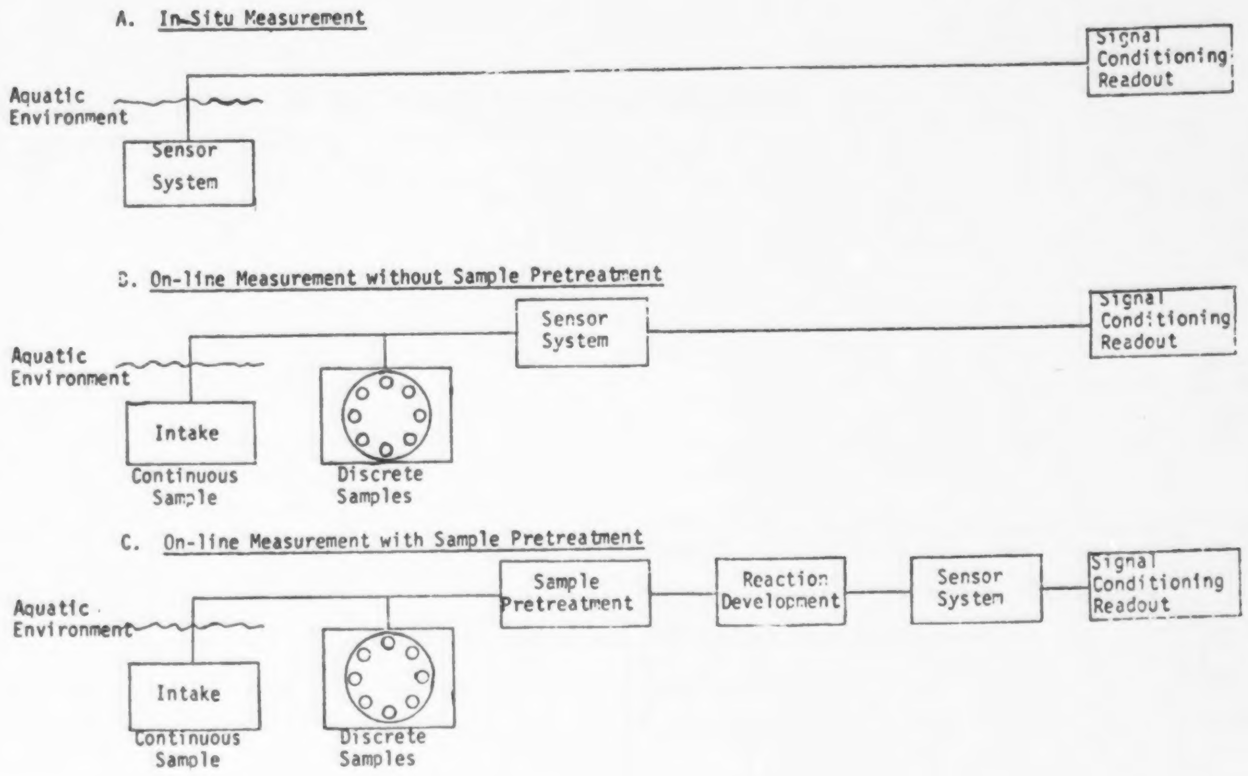

A. In-Situ Measurement
Aquatic Environment
Sensor System
Signal Conditioning Readout
B. On-line Measurement without Sample Pretreatment
Aquatic Environment
Intake
Continuous Sample
Discrete Samples
Sensor System
Signal Conditioning Readout
C. On-line Measurement with Sample Pretreatment
Aquatic Environment
Intake
Continuous Sample
Discrete Samples
Sample Pretreatment
Reaction Development
Sensor System
Signal Conditioning Readout

Figure 1. Automated measurement concepts

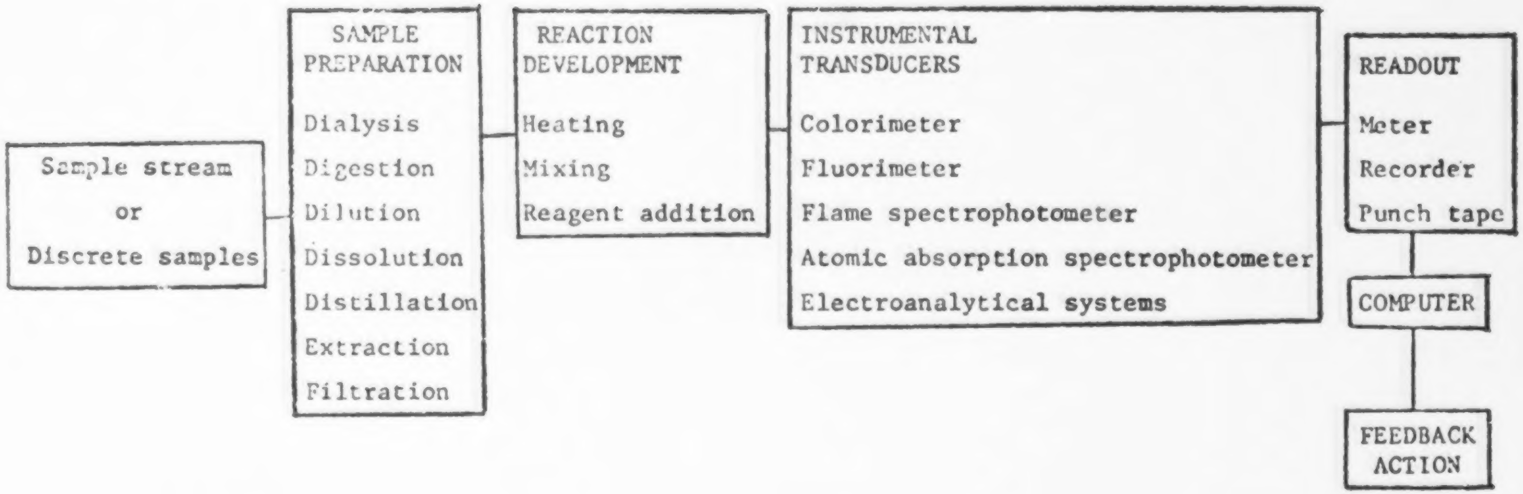
Sample stream
or
Discrete samples
SAMPLE
PREPARATION
Dialysis
Digestion
Dilution
Dissolution
Distillation
Extraction
Filtration
REACTION
DEVELOPMENT
Heating
Mixing
Reagent addition
INSTRUMENTAL
TRANSDUCERS
Colorimeter
Fluorimeter
Flame spectrophotometer
Atomic absorption spectrophotometer
Electroanalytical systems
READOUT
Meter
Recorder
Punch tape
COMPUTER
FEEDBACK
ACTION

Figure 2. Basic operations of continuous flow analysis

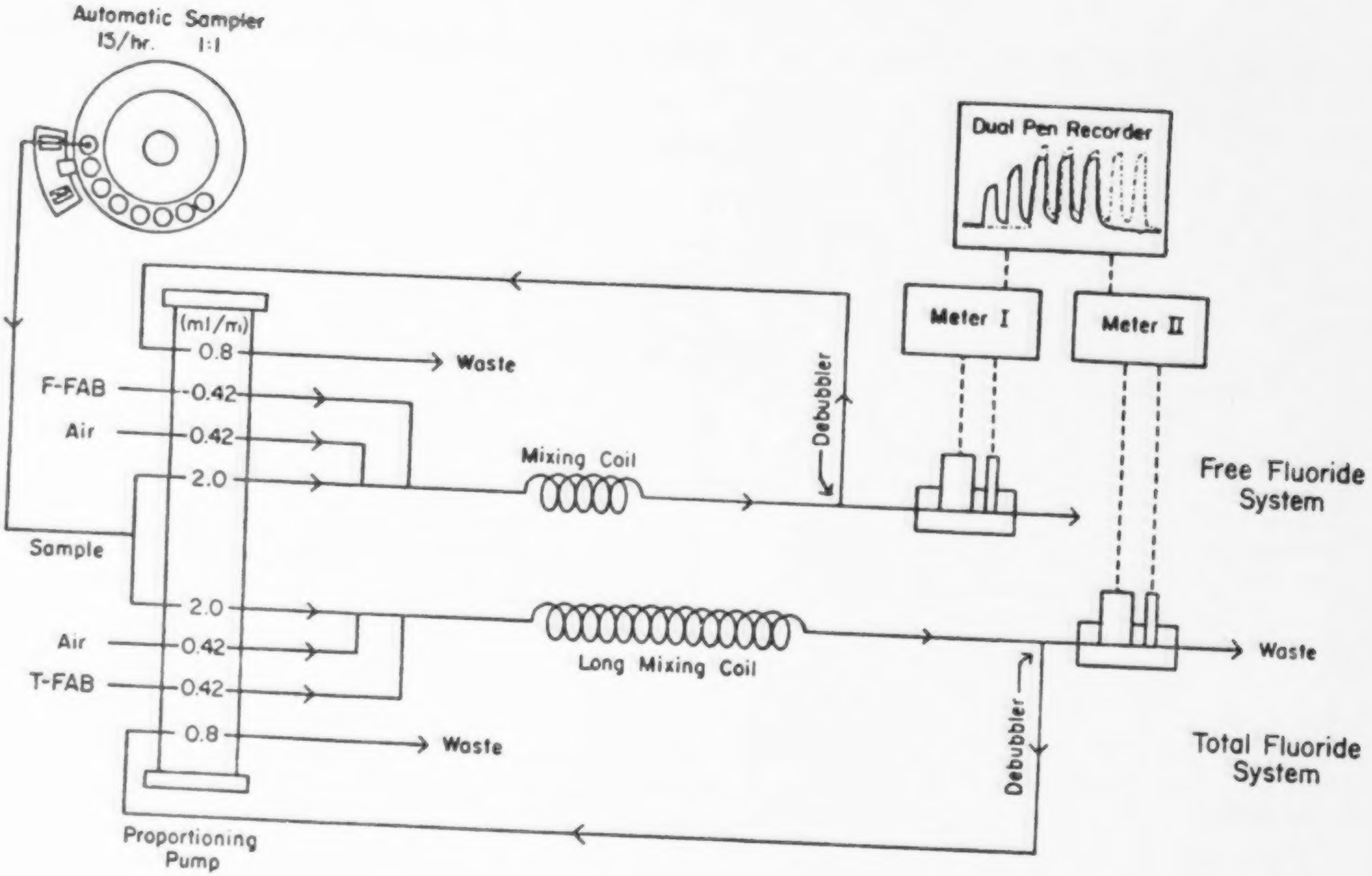
Automatic Sampler
15/hr. 1:1
Dual Pen Recorder
Meter I
Meter II
(ml/m)
0.8
0.42
0.42
2.0
2.0
0.42
0.42
0.8
Waste
F-FAB
Air
Sample
Air
T-FAB
Waste
Mixing Coil
Debubbler
Free Fluoride System
Long Mixing Coil
Waste
Debubbler
Total Fluoride System
Proportioning Pump

Figure 3. Schematic of automated sample analysis for free and total fluoride.

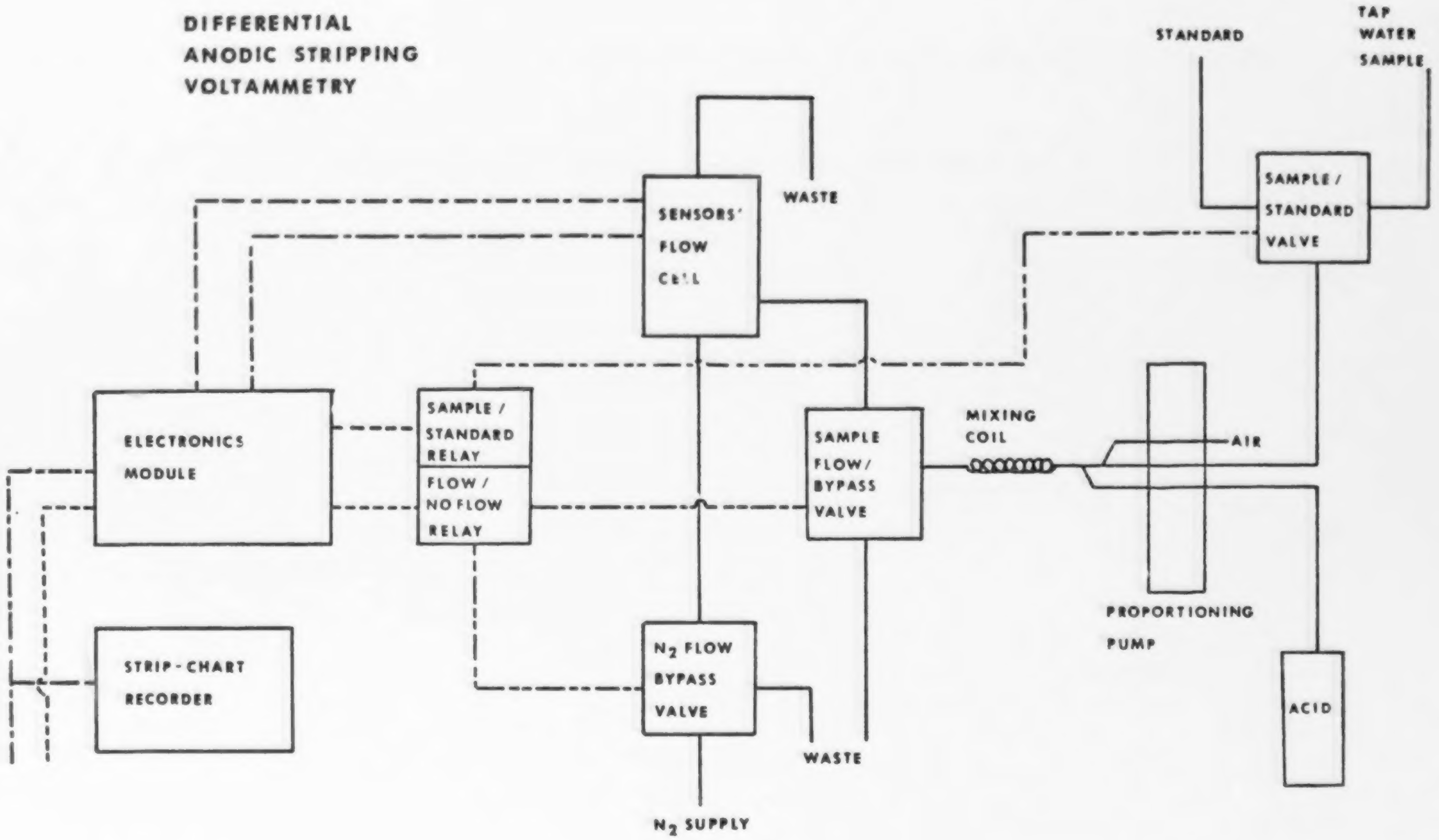
DIFFERENTIAL
ANODIC STRIPPING
VOLTAMMETRY
STANDARD
TAP WATER SAMPLE
SAMPLE / STANDARD VALVE
WASTE
SENSORS' FLOW CELL
ELECTRONICS MODULE
SAMPLE / STANDARD RELAY
FLOW / NO FLOW RELAY
SAMPLE FLOW / BYPASS VALVE
MIXING COIL
AIR
PROPORTIONING PUMP
ACID
STRIP-CHART RECORDER
N_2 FLOW BYPASS VALVE
WASTE
N_2 SUPPLY

Figure 4. Schematic illustration of trace metals monitor in the mobile laboratory.

A STATE VIEW OF THE NEED FOR RESEARCH IN IN SITU AUTOMATED WATER QUALITY SENSORS

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In looking for thoughts on which I could base my comments about the needs in sensor research and development, I came across a Request for Proposal from the USGS. It was issued on November 29, 1977, and it asked for the development of a prototype system to measure water stages and water surface velocity in natural streams on a continuous or time series basis using microwave techniques. Responses to this request were to be received in Washington no later than January 4, 1978, which makes it a very recent effort in sensor development. The objectives of the effort as stated in the RFP were to define, manufacture, test, and deliver a prototype system which would meet the following objectives:

- Operate unattended for a minimum of 30 days.
- Be capable of continuous or intermittent measurement of water stage and water surface velocity at programmable time intervals.
- Have no moving parts and no parts in contact with the water.
- Operate under a wide range of environmental conditions such as:
    1. Expected temperature range -30 to 130° F.
    2. Expected humidity range 0 to 95 percent.
- Be capable of measuring water stage with a resolution of ±0.04 feet over a range in stage of 20 feet. However, it would be most desirable to achieve a resolution of ±0.01 feet over a range of 50 feet. In this respect, be capable of mounting permanently at least 20 feet above minimum water surface.
- Be capable of measuring water surface velocity with an accuracy of ±4 percent for velocities ranging from 1 to 25 feet per second.
- Be as compact as practical consistent with a sound design.
- Be battery operated with minimal battery drain consistent with reliable and unattended operation.

I think the request emphasizes the need for automated in situ sensors of a very basic nature. Although this RFP may not be completely relevant to the objectives of this workshop (we are water quality oriented), it does put emphasis on the continuing need for this type of research and development. The design and evaluation of in situ sensors for environmental monitoring must be a priority area for agencies involved in the protection of our natural resoruces. My comments are, in a large part, upon experiences in south Louisiana, where stresses on the coastal environment have been noted for several decades, and based upon interaction with colleagues in the "scientific" community at LSU. It is appropriate that I stress the importance of the Louisiana environment and the activities which prompted a few of us at LSU to initiate reports in environmental monitoring and sensor development.

The coastal zone of Louisiana extends approximately to the 5-foot contour line at its northern boundary, west to the Sabine River and eastward to the Chandeleur Islands. The area is estimated to be about 10.5 million acres or 16,400 mi^2.

Marshlands comprise the bulk of the wetlands, some 4.2 million acres or 6,563 mi^2. These marsh acres support 10 million user-days of recreation per year. They also hold some 10,220 camps, which serve as away-from-home bases for a range of marsh activities, including fishing, hunting, and boating.

Further categorization of the marsh types shows that saline marshes account for 932,000 acres or 1,456 mi^2, freshwater marshes stretch for 1.3 million acres or 2,031 mi^2, while mixed marshes, being the most extensive, comprise roughly 2 million acres or 3,040 mi^2. Swampland accounts for about 1.6 million acres or 2,500 mi^2.

Thirty-one percent of the coastal region, or 5,279 mi^2, is surface water. Predominant water bodies include Timbalier, Vermillion, Caminada and Baratarta bays; and lakes Borgne, Salvador and Pontchartrain. Eight river basins together with a large number of manmade water features give coastal Louisiana a total land-water interface of 30,190 miles, second only to Alaska. The shoreline-gulf for the state is only 363 miles, the smallest of the land-water interfaces. Over 11,800 miles of navigable channels exist in the coastal zone. About 8,850 of these miles are located south of the gulf intercoastal waterway.

Tides in Louisiana are diurnal ranging from one half foot to a maximum of 2 feet. The average is slightly greater than one foot.

A great part of the environment described above has been created by government and private interests, namely the Corps of Engineers and the major oil companies. Their dredging activities account for many miles of the navigable waters. These activities continue and, in fact, are increasing due to the energy shortage. Further, there are relatively new developments in the coastal zone.

The Louisiana Offshore Oil Port, Inc. (LOOP), a consortium of major U.S. oil companies, has planned the construction of an oil terminal 18 miles off the coast of Louisiana to handle deep-draft supertankers. The port, its connecting pipelines and related land-based facilities will provide a means for supplying imported crude oil to refineries in southeastern Louisiana and in areas of the midwest, and will have a capacity to initially handle up to 1,400,000 barrels of crude oil daily. The oil port project, as proposed by LOOP, will consist of: 1) an offshore terminal for unloading deep-draft crude oil tankers, 2) large diameter buried pipelines from the offshore terminal to a booster station at the shore, then to an onshore storage facility, 3) the onshore storage facility itself, and 4) a pipeline from the onshore storage facility to the terminal of capline, one of the world's largest pipelines, located on the Mississippi River at St. James, Louisiana. Port construction is to begin in early 1978 with crude oil handling to commence by late 1979.

Another activity is the storage of oil in salt domes. There is already storage in three areas with proposed domes in Napoleonville and other areas suggested for use if pending investigations are successful. Once oil is stored in the subsurface reservoirs, there will be the ever-present possibility of leakage.

The Louisiana state legislature acknowledged the environmental problems that could be caused by a superport and its associated onshore facilities when it established the offshore terminal authority as the primary licensing and regulatory agency for the proposed Louisiana superport. The legislation creating the authority (LA. RS 34:3101-16) requires that protection of the environmental monitoring program is mandated, the purpose of which is to ascertain the existing ambient environmental conditions and then detect and evaluate any of the potentially deleterious effects the superport may have on the coastal environment during port construction and subsequent operation. This evaluation will form the basis for determining where, when and how necessary remedial measures are to be taken.

The Environmental Monitoring Program required by the enabling legislation includes assessing:

> The environmental stresses caused by oil spills and other polluting instances;

the air and water pollution levels in the Louisiana coastal environment;

the offshore water column and offshore benthos;

shoreline, estuarine marsh, and freshwater swamp vegetation and fauna;

the number, movement, and spawning and breeding cycles for wildlife in the Louisiana coastal environment;

saltwater intrusion;

water circulation and drainage; and

shoreline erosion and erosion along pipeline canals.

The list of environmental information needed to support the authority's monitoring program is both explicit and extensive and suggests the means used for acquiring the basic information must be:

accurate

long-term/reliable

cost effective

based on "real time" data

To meet the need for a comprehensive Environmental Monitoring Program which will satisfy the above criteria, a well planned, coordinated effort is required. The Louisiana Department of Wildlife and Fisheries has been analyzing water quality in the coastal zone for many years. The typical measurement technique is to go to the site by boat or helicopter, dip sensors into the water and record readings or take water samples back to the laboratory for analysis. While this is the only way that some data can be obtained, the cost is high, sampling is limited by weather and the data are not available on a real time basis. There are no "new" monitoring techniques proposed by the F & WL personnel.

A continuous in situ data acquisition system could provide a significant improvement in the present and planned monitoring program. Data from a real time system, through cooperation with the Department of Wildlife and Fisheries, would be analyzed to determine the relationships between changes in physical parameters such as temperature, salinity, dissolved oxygen, etc., and changes in plant and animal life. The in situ monitoring station would be used to sample those physical parameters found to be the most critical as often as needed (for example, on an hourly basis) and transmit the data to a receiving station. Analysis of these data would be used to determine where and when more detailed analysis of water quality was required. The insitu monitoring platform could also provide data on wind and currents which would be necessary to model regional dynamics. These models would be useful in predicting the movement and dispersion of pollutants, the flushing time of estuaries, etc.

The requirements that data acquisition in the environmental monitoring program must be provided in "real time" and be "cost effective" imply that measurements be made from unmanned in situ monitoring platforms. The areas of Louisiana, and, in fact, most coastal zones, are entirely too vast to continue operating in a bucket brigade mode. Platforms must be designed for operation in remote areas with power supplied from batteries and/or solar panels. Although the list which follows is not all-inclusive, it does represent those environmental parameters which would be desirable or useful in the characterization of an estuarine area. The parameters are grouped in order to facilitate this discussion. Those in Group I comprise the basic parameters found in many water quality analyzers such as those manufactured by Hydrolab, Martek, Beckman, etc. Sensors for measurement of temperature, salinity (calculated from conductivity), depth, and pH are relatively reliable for short periods of time. This is not the case for continuous measurements, especially for dissolved oxygen (DO). As pointed out earlier in this meeting, a major problem with this type sensor is fouling of the membrane. This reduces the permeability of the membrane which results in an apparent decrease in DO.

TABLE 1. DESIRABLE MEASUREMENT PARAMETERS IN ESTUARINE AREAS

GROUP I	GROUP II	GROUP III
Water Temperature	Current Velocity	Chemical Oxygen Demand
Salinity	Wind Velocity	Suspended Particle Concentration
Dissolved Oxygen	Evaporation	Chlorophyll *a*
pH	Rainfall	Hydrocarbon Content
Depth		Acoustical Signature Trace Metals Chemical Elements

Experience by personnel with the Corps of Engineers in New Orleans indicates that sensor degradation takes place rapidly in areas where the water is not fast moving and where the water contains oil and/or fine silt. The estuarine areas of Louisiana have precisely these characteristics. Therefore, development work is necessary to provide better sensing techniques or to adapt presently available sensors to make them suitable for continuous use in an in situ monitoring platform application.

In the summer of 1977 we initiated an experimental effort designed to measure the error in recordings from in situ water quality sensors. The sensors were located in a range of environmental conditions from fresh water to sea water.

Two sets of data were recorded simultaneously at all experimental locations. The experimental data set consisted of readings taken from in situ sensors, and included the measurement of dissolved oxygen, conductivity, pH, temperature, and depth. The control data set was obtained by measuring the same parameters with auxiliary instruments. A set of differences was produced over a 2-week period which represented the error caused by environmental degradation of the in situ sensor. After the 2-week period the unit was removed from the water column and prepared for deployment in the next experimental site. Preparations for deployment included inspection of the assembled instrument, disassembly and inspection, cleaning, reassembly, and calibration. Several methods of statistical analysis are being used in analyzing the data sets. For instance, simple regression analysis is being used to determine the rates of error inducement for a location in a time period.

We can make several recommendations for research efforts based on biofouling alone since this does appear to be a prime factor affecting the longevity of sensor stability. Several approaches to this problem would include:

- Modifications of the sensor to restrict light.
- The development and utilization of anti-fouling agents which inhibit biological growth, and
- The development of new probes which will be resistant to fouling of all kinds. This would call for basic research in materials science.

Physical factors which were observed to affect hydrolab control in water columns were tides, waves, and bottom sediments.

Parameters in group II describe some of the driving forces which cause changes to take place in the other parameters. They are also useful in developing models to predict the movement and dispersion of pollutants as well as various living organisms. (The sensor to be developed by the USGS RFP could very well be placed in this category.) Correlation of these parameters with others can significantly improve the understanding of the complex forces at work in the estuarine area. For example, knowing rainfall, wind velocity and evaporation rate would be useful in explaining and predicting changes in salinity and dissolved oxygen. Relatively little development work on sensors for this group is anticipated; however, signal conditioning and interface circuits must be designed and tested.

The parameters in group III are those for which major development work is needed. At present there are no field instruments for in situ monitoring of chemical oxygen demand (COD). This parameter is generally determined by taking water samples and returning to the laboratory for analysis. Suspended particles are usually detected by optical techniques employing a light source and lenses. Fouling of the optical components is a major problem. One chlorophyll sensor using a filtered fluorometer was incorporated in a water quality indicator system developed by Magnavox for the NOAA data buoy office. The system was developed in 1975 and has been used only on a limited basis. There are sufficient data to evaluate the applicability of this sensor to the estuarine environment. It is anticipated that fouling of the optical system will again be a major problem. There is no in situ sensor for detecting hydrocarbon content in the water or for detecting a thin layer of oil on the surface. Large oil slicks can be detected by remote sensing; however, small amounts of oil are difficult to detect, especially when emulsified in a surf zone and then carried into the estuarine area.

There are other parameters which will require monitoring that are very difficult to measure and will require intensive work in the R and D sector before continuous in situ measurements can be made. These include BOD, heavy metals, pesticides, toxic chemicals, petroleum products in general, and others.

These deficiencies emphasize a need for basic research and the development of new approaches to monitoring systems.

If we take the definition of water quality to be the capability of supporting both plant and animal life, then it can be used as a basis for suggesting areas of potential sensor research.

Support of plant and animal life implies two important ideas: (1) the required elements are present in sufficient quantity; and (2) these elements have been combined into the proper molecular structure for use in normal metabolic processes. The latter implies that some molecular structures of the same elements may indeed produce abnormal physiological processes if used as metabolites by a living system. It is felt that less than sufficient attention has been focused on the second idea, molecular combination of elements integral to our water sources.

In particular it has been suggested by Professor F. Warner, Louisiana State University, that basic research be undertaken to develop water sensors capable of providing some structural information about biological trace metal (lead, zinc, selenium, copper, iron, cadmium, platinum, etc.) complexes inherent in water sources. New knowledge gained from present biophysical research (investigation of iron and platinum in malignancy) clearly shows that there are three basic reasons for abnormal biological development in the presence of trace metals: (1) the presence of the element itself; (2) if present, the molecular structure of the metal-containing complex; and (3) the quantity of metal complex available for biological reaction. For example, we have found, from a study of platinum binding to serum proteins, that several complexes could be formed depending on the reacting metal complex and the quantity of the complex present. The protein complexes formed ranged from primary binding of platinum to transferring to forming polymers of albumin. In a recent issue of the journal, "Clinical Chemistry," the problem of reactions between platinum chemotherapeutic complexes and serum proteins was exposed and lack of knowledge concerning the bio-structure of these secondary complexes was discussed. It is obvious that there needs to be additional work done to identify not only elements present but, just as important, the chemical complexes formed from these trace metals.

As an initial research subject for development of sensors to abstract some chemical structural data, on line, Professor Warner suggests that consideration be given to nuclear magnetic resonance spectroscopy. What is involved here is developing a small flow-through spectrometer to look at chemical shifts in carbon, nitrogen, or hydrogen, such as those used currently in measuring in vivo blood flow. The transmitted data could then be compared with known spectra generated by metal-containing complexes. Since magnetic resonance is a phenomenon dependent on molecular magnetic fields, further information may be obtained by photo excitation or paramagnetic electrons during NMR examination.

There are numerous physiochemical processes that may, indeed, provide the basis of water quality determination in the future, but the time is now to accomplish the basic research. Of utmost importance in this research will be the investigation of innovative techniques for taking advantage of physiochemical processes.

Professor Jim Robinson, Louisiana State University, has suggested that we develop a package for monitoring turbidity on a continuous basis by using a deuterium light source which is quite stable and a detector. Monitoring would be accomplished by measuring the intensity of radiation reaching the detector.

A second area of interest to Professor Robinson would be in monitoring of oils and greases by using a source of infrared radiation and monitoring a reasonably narrow wavelength region which is typical of oils and greases. This would not be difficult to do and is well within our capability to demonstrate.

A third area of great interest would be in the monitoring of heavy metals. Most of the available sensors in this area are based on electrochemistry and they break down in practice because they determine only the ionic concentration rather than the total metal concentration. We feel that some development work should be carried out in this area as a priority item.

These are certainly not the only areas open for good research and development projects. There is a continuing need to upgrade power sources, microprocessing techniques, and communication linkages.

ELECTROCHEMICAL TECHNIQUES IN WATER QUALITY EVALUATION

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Modern electrochemical analytical techniques applicable to the assessment of water quality may be divided into six classes: conductivity, potentiometry, amperometry, coulometry, chronopotentiometry, and voltammetry. These procedures are based on either an evaluation of the thermodynamic state of the water system or on a measurement of transport properties. The quantity ultimately measured is either resistance, emf (voltage), time, or current. Some of these techniques are simple and adapted with relative ease to both field use and automation, while others demand elaborate equipment and are better suited to the laboratory (1).

Conductivity is a classic technique for the routine and rapid examination of overall water quality. The measurement is easily performed in the field and is a superior technique for the determination of salinity. Accurate conductivity measurements may be used as a check on the gross accuracy of a water analysis. Nevertheless, conductivity is nonspecific, reflecting the sum total of ionic impurities in the sample and ignoring the presence of nonionic solutes such as soluble organic material.

As applied to water analysis, potentiometry has already proved highly useful and further applications of this technique appear highly promising. Measurements of pH utilize the emf developed between a glass electrode and a reference electrode to assess the level of hydrogen ion activity or concentration and the alkalinity of the sample. The newer ion-selective electrodes, which are now available for some 20 different ionic species, enable the method to be extended to the routine evaluation of other important parameters such as the concentrations of sodium, chloride, ammonium, fluoride, lead, copper, sulfide, and cyanide ions. Water hardness can be measured by this method, and simple modifications permit the level of dissolved carbon dioxide to be established.

The measurement of emf with highly sensitive digital voltmeters is simple and readily made in the field. Temperature regulation need not be elaborate, but specially designed flow cells may be needed, plus some provision to avoid contamination with atmospheric carbon dioxide. The emf responds in logarithmic fashion, and thus the method becomes more sensitive as the concentration decreases.

In spite of their versatility, potentiometric methods are not without their drawbacks. The emf responds to the activity of the ionic species rather than to its concentration. Furthermore, serious errors may be involved if liquid-junction potentials at the reference electrode are not balanced out of use of calibration standards which match closely the ionic strength of the water sample. This objective is difficult to achieve at the present time, and further study of this problem is needed. Finally, no electrode is perfectly selective, and care must be taken to avoid interferences; for example, for the accurate estimation of the concentration of sodium ion, the concentration of this ion must be at least a thousandfold greater than that of the hydrogen ion in the solution.

In amperometry, a steady-state current is measured and related to the concentration of an electroactive substance. A polarizable electrode (dropping mercury electrode or rotating platinum electrode) is used, together with an external applied voltage so chosen that the limiting current is proportional to the concentration of the species to be measured. A simple circuit utilizing a microammeter to measure the current may be suitable for the highest accuracy. The need for an external source of potential can be avoided by choosing electrodes such that a constant potential is developed within the cell.

The amperometric determination of dissolved oxygen in the field is highly satisfactory, and commercial instrumentation is available for this purpose. Modifications more suitable for laboratory use permit chemical oxygen demand and total oxygen demand to be evaluated. An instrument applying amperometry to the estimation of chlorine residuals in the field has been described (2). Its sensitivity appears to be a few parts per billion. Iodine released from a KI reagent by the dissolved chlorine is determined amperometrically. Amperometric procedures can also be modified to permit the separate estimation of chloramines.

Coulometry and chronopotentiometry are highly precise techniques, adaptable both for major constituent analysis and for trace analysis. Nevertheless, their automated application in the field appears limited.

Voltammetric methods of analysis depend on the current-voltage relationships at a polarizable electrode. The many variations include conventional polarography, square-wave and pulse polarography, cyclic voltammetry, and anodic stripping techniques. The latter procedure is a highly sensitive trace analytical method, especially for the estimation of metal ions. Its application in monitoring water quality is discussed in detail by another participant in this workshop. Voltammetric methods are useful for determining aluminum, arsenic, cadmium, copper, lead, and mercury, as well as certain anions, notably the halides, cyanide, sulfate, and sulfite. Sometimes separations are required, however, which render these techniques time-consuming and poorly adapted for automated field use.

A complete monitoring system for following the technological process of surface water treatment of Danube raw water has recently been described (3) and is under further development. The data acquisition system uses 15 sensors with analog outputs and 7 instruments with digital outputs. The physical and chemical properties monitored are flow rate, temperature, turbidity, pH, pCl, conductivity, chemical oxygen demand, alkalinity, hardness, and free chlorine.

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(3) T. Cserfalvi, T. Meisel, B. Tarnay, K. Seybold, F. Galina, and E. Pungor, Z. Anal. Chem., 282, 351-355 (1976).

WATER QUALITY SENSOR TECHNOLOGY USING ACOUSTIC TECHNIQUES

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Introduction

This talk will emphasize an acoustic method of sensing the thickness of an oil layer floating on the top of either fresh or salt water. The system is capable of functioning in quite rough sea conditions because of the effective employment of a microprocessor. Some mention will be made of other situations in water quality sensing wherein accoustic techniques offer some unique advantages in comparison to any other device.

Oil Thickness Sensor Description

An early model of the acoustic oil thickness sensor was developed in 1974 without the incorporation of a microprocessor. The first system served to establish the validity of the technique even though it required taping large amounts of acoustic data for subsequent processing on a lab computer. The most notable disadvantage to this first system was the turnaround time required between taking the test data and reading out the layer thickness as a function of time.

Figure 1 is a photograph [Note: Photographs are not reproduced in this report] showing a typical oil management test wherein the Sonar Oil Thickness Sensor (SOTS) was employed for the first time off the California coast. Figure 2 is a photograph of an oil recovery device in a test performed by the U.S. Coast Guard. Measurement of the actual oil layer thickness both inside and outside the recovery device is the most important measurement of all.

Figures 3, 4, and 5 outline the system evolution, output capabilities and data retrieval capabilities. Figure 6 shows a block diagram of the buoy SOTS system. The SOTS electronics is little more than a refined acoustic Fathometer used to sense the water depth from a boat by acoustic means. The SOTS transducers are small commercial acoustic devices which are resonant near the frequency of 1-MHz. One transducer radiates a short acoustic pulse and the other receives the total acoustic echo from any acoustical reflectors located above the transducer. These echoes are highly amplified and the microprocessor seeks out the specific echoes of concern from both the underside and the top side of the oil layer It is the travel time difference between these two echoes which corresponds to the oil layer thickness.

SOTS Output

There are three crucial points that should be mentioned because of their importance to the ultimate performance of the SOTS. The first is the convenient physical fact that because of the acoustical geometry, the first echo (from the underside of the oil surface) is the weaker of the two acoustical echos. This means that even a very high intensity from the top of the oil surface cannot "mask" or override the weaker echo.

The second major point is that even though a rough sea surface can have a relatively large tilt relative to the horizontal, the acoustic system can still function. This is because a steep wave slope is both preceded and followed by a wave crest and a trough,, both of which have essentially zero slope. Finally, the microprocessor memory makes it simple to ride smoothly over these echo "drop outs" without losing important thickness information.

The microprocessor makes it possible to focus on any one of a large variety of output oil thickness parameters. Figure 15 illustrates this point and a typical parameter of interest to the system user might be the average oil layer thickness at the SOTS transducer location for the immediately preceding 5-minute period. The microprocessor makes it possible to change to any other parameter such as the highest value of layer thickness during a particular time period of a test. One might be more interested in the oil thickness RMS value or its variance during a particular time period.

Controlling the SOTS buoy system underutilizes the Motorola 6800 microprocessor so that other functions may be handled by its reserve capacity. One of these is the pre-conditioning of data and even the storage of data over considerable time periods. This stored data might be rapidly extracted from a disk or tape file (i.e., by satellite) or recovered when the buoy is retrieved from its field station.

Figure 7 shows the ultimate oil layer thickness sensing resolution limit as it depends upon the selected acoustic frequency. The ultimate best use for the SOTS is in measuring the thickness of significant oil layers rather than in detecting a very thin oil sheen on the surface of the sea or within an estuary. Optical techniques would appear to always have the advantage over acoustics in this thin film case. However, at about perhaps 1/2 mm and on up to many cm, the acoustic technique would probably be the best possible approach that is available.

Conclusions

Figure 8 shows in an elementary way some other regions where acoustic sensing can be of unique value in water quality sensing applications.

Perhaps the most important two of these would be in the detection of suspended particulate (sediment) matter and in the detection of flow profiles. The "scatter cross-section" for optical energy in the atmosphere depends upon the data. The bucket dipping, weighing, drying technique applied to measuring particle size distribution is indeed crude, time consuming, and costly. Conventional current meter arrays are very expensive, even if they would have a chance to survive in the violent debris-laden run of a river in the spring.

EVOLUTION

GENERATION	
1	- AFTER THE FACT PROCESSING AWAY FROM COLLECTION SITE - STATISTICS COMPUTED BY HAND MEASUREMENT
2	- REAL TIME PROCESSING - STATISTICS COMPUTED BY HAND MEASUREMENT
3	- REAL TIME PROCESSING ON SITE - STATISTICS COMPUTED REAL TIME WITHOUT ADDED ERRORS DUE TO MEASUREMENT BY HAND

Figure 3. SOTS system evolution

OUTPUT CAPABILITIES

REAL TIME MONITOR

TELETYPE - FULL MESSAGE CAPABILITY

7 SEGMENT LEDS - LIMITED MESSAGE CAPABILITY

ANALOG - METER - NO MESSAGE CAPABILITY

STORAGE MODE

DIGITAL - MAGNETIC TAPE
PUNCH TAPE
DISK

ANALOG - STRIP CHART
MAGNETIC TAPE

Figure 4. SOTS output capabilities.

DATA RETRIEVAL

BASIC SYSTEM

- OIL THICKNESS VS. TIME
- BAD DATA DETECTION

EXTENDED SOFTWARE SYSTEM

- MAXIMUM THICKNESS
- MINIMUM THICKNESS
- MEAN THICKNESS
- THICKNESS VARIANCE

EXTENDED HARDWARE SYSTEM

- NAVIGATION/LOCATION
- OIL REFLECTION COEFFICIENT

Figure 5. SOTS data retrieval capabilities.

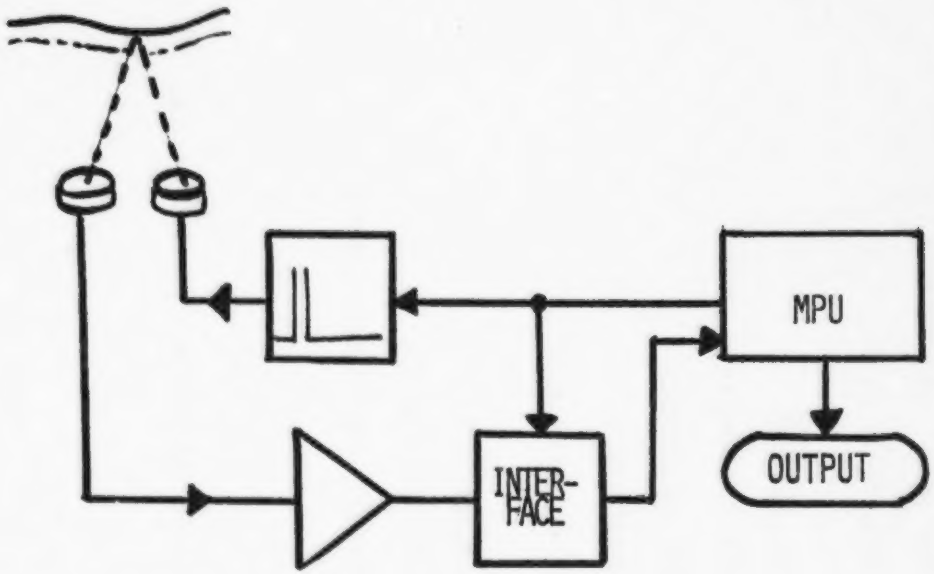
MPU
INTER-
FACE
OUTPUT

Figure 6. SOTS block diagram

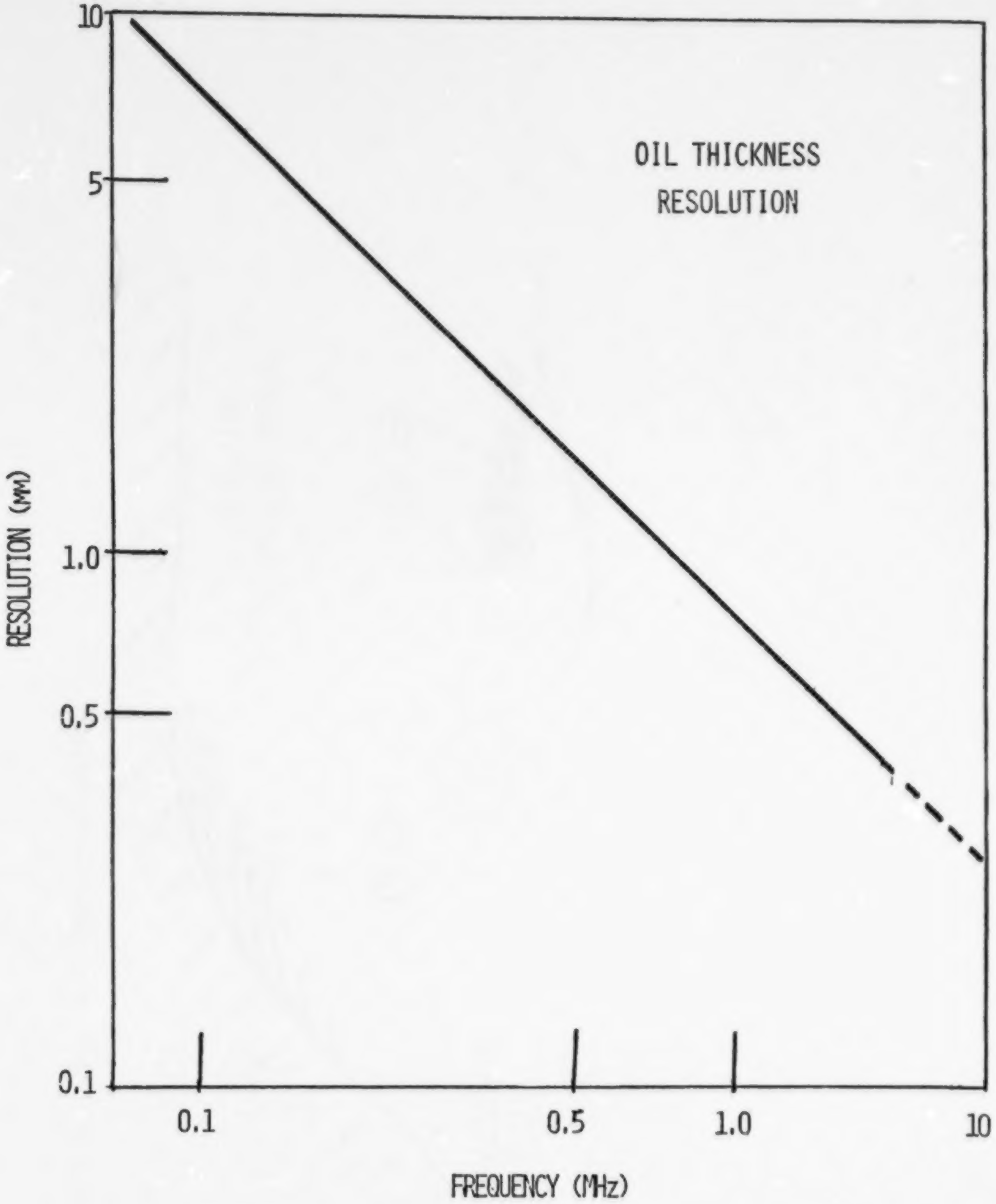

Figure 7. SOTS oil thickness resolution

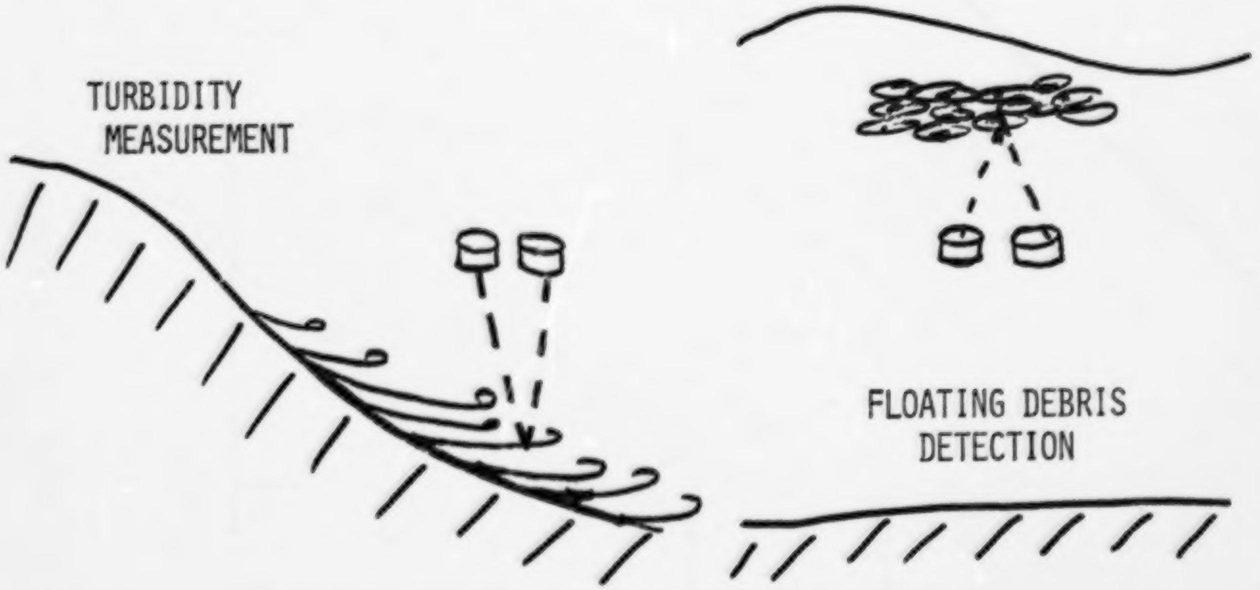
TURBIDITY
MEASUREMENT
FLOATING DEBRIS
DETECTION

Figure 8. SOTS alternate applications

WORKING PANEL REPORTS

This section contains the reports prepared by six Working Panels at the Workshop. The panels consisted of a Measurement (Sensor) Needs panel which addressed Federal agency water quality measurement needs that might be met by in situ sensor technology, four Sensor Technology panels which reviewed specific sensor areas in terms of applicability to automated in situ deployment, and a Needs and Technology Integration Panel which correlated and summarized the outputs of the needs and technology panels. Panel titles and their chairmen, in order of presentation on the following pages are:

Measurement (Sensor) Needs	Clifford Risley, EPA
Electrochemical Sensor Technology	Richard A. Durst, NBS
Electrophysical Sensor Technology	James H. Ficken, USGS
Optical Sensor Technology	Vincent G. Di Pasqua, USCG
Automated Wet Chemical Sensor Technology	Harlan L. McKim, COE
Needs and Technology Integration	Barbara S. Pijanowski, NOAA and John D. Koutsandreas, EPA

The first five panels met concurrently during the last one and a half days of the Workshop; the last panel deferred deliberations to the day following the Workshop since it needed reports from the other panels to complete its work. The last panel consisted of chairmen from the other five as well as other interested participants.

In order to approach discussions in a preplanned, systematic and somewhat uniform manner, the chairmen participated in preworkshop meetings to design panel discussion topics and formats. Various ideas on sensor category breakdowns were explored by the workshop planners and consultants before selecting the four technology categories used in the Workshop. Recommended individuals were recruited as panel chairmen and draft discussion topics and outlines were reviewed and drafted. All chairmen met several weeks before the workshop to exchange ideas and to develop uniform approaches to panel discussions and reporting. This preworkshop preparation proved to be valuable in minimizing confusion. (The panel chairmen are to be commended for their extra effort and dedication in preparation for the Workshop.)

Once involved in the deliberations at the Workshop, panel chairmen found it necessary to modify slightly the "standard format" for written reports in order to accomodate their specific breakdown of sensor categories. Panel reports are presented on the following pages. In compiling these reports, limited editorial license has been exercised in an attempt to provide further similarity and uniformity in the writings contributed by numerous authors and chairmen. Complete uniformity was not achieved or sought in order to preserve thoughts and philosophy as reported.

The Panel membership is listed in the beginning of each panel report. All Workshop attendees (see the roster at the end of this report) were requested to specify their interests for panel participation. As much as possible, within the limits of balancing panel membership, assignments were made according to these desires.

MEASUREMENT (SENSOR) NEEDS: Working Panel Report

Members

Clifford Risley, EPA, Chairman
Olin D. Bockes, USDA
Richard W. Paulson, USGS
Charles R. Eastwood, NASA
Earl E. Eiker, COE
Victor W. Lambou, EPA
Enrico Mercanti, NASA
Nelson L. Milder, NASA
Charles A. Whitehurst, Louisiana State University
Mary S. Hunt, University of California
Paul C. Etter, MAR Inc.
Leslie G. McMillion, EPA
Barbara Pijanowski, Chairman of the Integration Panel, spent considerable time with this panel.

Summary

This workshop has brought together representatives of a number of agencies who have considerable experience and requirements for monitoring water quality. All are in agreement that the need for monitoring is increasing exponentially and that Federal agencies are frustrated by their inability to expand their monitoring efforts sufficiently to keep up with the demand. No agency has sufficient manpower to provide the required monitoring effort using the traditional approach of field sampling and laboratory analysis. There is complete agreement that we must develop automated monitoring systems that can measure the parameters of need, with accuracy, simplicity and reliability.

There is also concurrence that we have an already demonstrated ability to build reliable in situ monitoring systems which have operated dependably for weeks at a time with reliable sensors, data control packages, memory units and recording on tape.

Also, automated field record and field data memory units which dump data to satellites or telephone lines are well developed and used by several agencies.

The major problem with present systems is that so few reliable sensors exist. It is readily apparent that the availability of only a few reliable sensors for field applications is the primary constraint on the application of automated monitoring to the management of water quality and water resources. Many of the needed parameters cannot now be sensed automatically. High priority must be placed on sensor development.

The panel recognized that for some of the parameters of interest, we do not have good analytical procedures in the laboratory. We feel that the effort to develop good field sensors will have a payoff benefit to the laboratory as well.

An important part of the automated monitoring package should be a sample collection component which can be triggered to collect samples when the sensors detect pollution levels in excess of prescribed limits.

The panel also found that there may be excellent opportunities for reducing the costs of obtaining and analyzing groundwater samples by use of automated in situ devices. These devices, once installed, would reduce the time and cost that is entailed by field personnel going to the well sites, setting up pumping equipment over each well, obtaining the samples and transporting them to the laboratory for analysis.

The automated devices could be selected for determination of key parameters, installed and occasionally serviced in conjunction with water-level measuring devices which are generally installed in the present operational scheme.

State and Federal Agencies need automated monitoring:

- Spill alerts, ocean, lake and river
- Lake monitoring, where spill potential exists
- Estuary monitoring, where spill potential exists
- Ocean monitoring, shipboard and buoy
- In-stream monitoring for water quality trends

- Ocean monitoring, shipboard and buoy
- In-stream monitoring for water quality trends
- Wells and ground water supplies
- Short term intensive studies for enforcement actions
- Within the soil mantle
- Data for water quality model development
- Data for planning corrective actions
- Data to support best available technology (BAT) requirements for 129 Toxic Compounds
- Municipal waste treatment plant effluent permit compliance
- Industrial waste treatment plant effluent permit compliance
- Rural and urban runoff characterization
- Storm and combined sewer overflow measurement
- Data to determine long term toxic buildup
- Data to develop land use relationships
- Nonpoint source water pollution monitoring.

State and Federal Agencies also need emergency response capability. They need to move out to a field site via helicopter or other rapid transport to define affected areas and determine the concentrations of pollutants and assess the seriousness of the incident. Action must be taken to confine the pollution, alert and protect the public and take corrective action. Rapid intensive monitoring is necessary to make these decisions and to measure the effectiveness of corrective actions after they are taken.

Monitoring for the above needs requires that automated devices and their sensors be able to perform at the water surface, subsurface at many depths (ocean, lakes, rivers and groundwater) referenced to water surface and to bottom surface, on the bottom and at various depths in the soil mantle. The devices must also work in a temperature range from 0 to 40°C, and must be resistant to fouling by bacteria, algae, sediment, and chemical corrosion. They must also withstand physical disturbance from currents and wave action.

The Measurement Needs Panel decided that it should concentrate its efforts on the development of a list of parameters for which the greatest present need and anticipated near-term needs exist. The parameter list which the panel developed was grouped into three categories and is attached to this panel report (Table 1).

Group 1	Parameters of need to all agencies (state, federal and private).
Group 2	Water quality indicators needed by many agencies but carrying less concensus among agencies as to importance ranking.
Group 3	Water quality indicators of specialized importance to some agencies but not of high importance or concern to all agencies.

We see a great need to further develop these needs by having each agency user group address the parameter list to determine its own applications and requirements. We propose that a committee be appointed to make this survey and that the return information be made available for use by a subsequent interagency water quality sensor workshop.

General Requirements for All Sensors and Systems

Reliability and Quality Assurance -- Due to the increase in costs of travel and manpower, and the need for monitoring data, our goal would be to have sensors with a 60-day station life-time and up to 6-month time interval between maintenance. The type of sensor will largely determine the possibility of realizing this goal.

Other desired goals:

- Longevity (3 to 5 years or longer).
- Mean time between failure or service cycle (resupply of reagents, filters, etc.) (3 months to 1 year).
- Cost of sensor less than $1,000 each in production of greater than 1,000 units/year.

Complexity -- The sensors should be kept as simple as possible; should be modular, plug in, easily replaceable.

Operation and Maintenance -- Sensors should operate unattended for a 60-day maintenance schedule. Maintenance should be performed by one person in the field with little equipment necessary.

Modular components must be small enough to be replaced in the field.

Accuracy -- This is dependent upon the parameter under consideration, environment, considered applications, frequency of measurements.

Conclusion -- In conclusion the Panel wants to reemphasize its previous statement that we see a great need to further develop these needs by addressing the parameter list to each agency user group to determine their applications and requirements. We propose that a committee be formed to make this survey and that the return information be made available for use by a subsequent interagency water quality sensor workshop.

TABLE 1. HIGH PRIORITY MEASUREMENT NEEDS

Group 1 - Needs of all agencies (state, federal, and private)

- Temperature
- Depth
- Water velocity and direction
- Dissolved oxygen
- Conductivity (fresh water)
- pH
- Optical properties
- Density (sea water, ground water)
- Suspended particles (concentration, size, distribution)

Group 2 - Needs of many agencies

- Total dissolved solids (fresh water)
- Oil presence (visible sheen 1-3 micron)
- Oil quantity
- Phytoplankton biomass (chlorophyll a)
- Total phosphorus
- Dissolved phosphorus
- Available nitrogen
- Organic carbon
- Dissolved organic carbon
- Chlorine - wastewater

Group 3 - Specialized needs (of major importance to some agencies, but not to all agencies.)

- Chloride - fresh water
- Coliform
- ATP
- BOD
- Viruses
- Sulfate, Sulfides
- Zooplankton
- Metals*
- Pesticides/insecticides (herbicides)*
- Hydrocarbons
  - Aromatics*
  - Industrial solvents*
  - Phenols*
  - Benzene toluene group*
- Miscellaneous compounds*
- Radioactivity (gross α, gross β, gross γ)
- Ozone (fresh water)

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*See Table 2

TABLE 2. GENERIC GROUPING OF 65 SETTLEMENT AGREEMENT TOXIC SUBSTANCES*

Pesticides/Insecticides

- Aldrin/Dieldrin
- Chlordane and metabolites
- DDT and metabolites
- Endosulfan and metabolites
- Endrin and metabolites
- Heptachlor and metabolites
- Isophorone
- Toxaphene
- 2,3,7,8-Tetrachlorodibenzo-para-dioxin

Metals

- Antimony and compounds
- Arsenic and compounds
- Beryllium and compounds
- Cadmium and compounds
- Chromium and compounds
- Copper and compounds
- Lead and compounds
- Mercury and compounds
- Nickel and compounds
- Selenium and compounds
- Silver and compounds
- Thallium and compounds
- Zinc and compounds
- Iron
- Manganese
- Calcium
- Magnesium
- Potassium
- Silicon

Aromatics

- Polynuclear aromatics
- Polychlorinated biphenyls (PCB)
- Napthalene
- Chloronated Napthalene
- Phthalate esters

Industrial Solvents

- Carbon tetrachloride
- Chlorinated benzenes
- Chlorinated ethanes

(Continued)

TABLE 2. (Continued)

Chloroakyle ethers
Chloroform
Dichlorobenzenes
Dichlorobenzidine
Dichloroethylene
Dichloropropane and dichloropropene
Haloethers
Halomethanes
Hexachlorobutadine
Hexachlorocyclohexane (all isomers)
Hexachlorocyclopentadiene
Tetra chloroethylene
Trichloroethylene

Phenol Family**

Chlorinated phenols
2-Chloro phenol
2, 4 Dichlorophenol
2, 4 Dimethylphenol
Nitrophenols
Pentachlorophenol
Phenol

Benzene Toluene Group

Benzene
Benzidene
Dinitro-toluene
Ethyl benzene
Nitro benzene
Toluene

Miscellaneous

Acrolein
Acenaphthene
Acrylonitrile
Asbestos
Cyanides
Diphenylhydrazine
Fluoranthene
Nitrosamines
Vinyl chloride
Fluoride

**Not part of Settlement Agreement list. Added by Working Panel.

*From Consent Decree between Natural Resources Defense Council and U.S. Environmental Protection Agency, June 7, 1976.

OPTICAL SENSOR TECHNOLOGY: Working Panel Report

Members

Vincent G. DiPasqua, USCG, Chairman
Richard W. Newton, Texas A&M University
William H. Kirchoff, NBS
Eduardo D. Michelena, NOAA
Robert F. Middelburg, USGS
Jack A. Salzman, NASA
Frank A. Schiebe, USDA

Summary

This panel considered a number of optical techniques including passive and active spectroradiometry, transmissometry, and polarimetry. Some of these techniques do not require direct contact with the water and, as a result, require less maintenance than water contact sensors. All are dependent upon electromagnetic radiation from the water bodies. They can be made to scan large areas, and provide synoptic measurements. The active systems and some passive are capable of performing measurements night and day. Water parameters which can be detected include temperature, water velocity, optical properties, suspended particles, salinity, oil presence and quantity, sedimentation, turbidity, and chlorophyll a. The quantification of suspended sediments and oil presence has been demonstrated by lidar polarimetry. Spectrographic techniques could be developed to identify the more complex pollutants such as pesticides and hazardous materials. Differential radiometry can be used to measure chlorophyll concentration and turbidity.

Sensor Technology

Definition of Technology--

There are a number of optical in situ and near in situ water quality sensors now available. Many of these devices use the same measurement technique. As a result, it was decided to group the measurement concepts into several broad classes and subgroup specific sensors within the appropriate measurement concept class. The general classes of measurements considered were:

CATEGORY I: Passive Spectroradiometric
- a. on site non-contact
- b. in situ

CATEGORY II: Active Spectroradiometric
- a. on site non-contact

CATEGORY III: Transmissometers
- a. artificial broadband light source (transmission, 90% scatter)
- b. artificial narrowband coherent light source (forward scatter, 90% scatter)
- c. natural light source (index of refraction)

CATEGORY IV: Lidar Polarimeters
- a. on site non-contact
- b. in situ

Advantages--
- many optical sensing techniques do not require contact with the water; measurements can be made from a distance
- capable of scanning large areas to provide synoptic measurement
- maintenance requirements are less for those sensors not in water contact
- pretreatment of samples is not required
- provides the capability of multi-parameter measurements
- active systems are available 24 hours per day

Disadvantages--
- fouling of the lens
- susceptible to other radiation source
- passive systems have daytime limitations

Detection Capabilities--

Group I
- a. temperature
- b. water velocity
- c. optical properties
- d. suspended particles
- e. salinity

Group II
- a. oil pressence
- b. oil quantity
- c. phytoplankton biomass (chlorophyll a)

Group III
- a. potential to detect many items listed via spectrographic techniques

Near-Term (5-year) R & D Recommendations--

Emphasis should be placed on anti-fouling engineering and miniaturization and size reduction of existing sensor systems. These sensors which detect suspended particles should be advanced to operational field use as soon as possible.

Long-Term R & D Recommendations--

All sensors require improved reliability and precision. Many sensors have multi-scanning detection capability that needs to be developed over a long time period. This is particularly true of microwave spectroradiometry.

Remarks and Conclusions--

Optical properties, water turbidity, oil detection and salinity are now detectable, and to a certain extent quantifiable measurements can be made by existing sensors. We still are unable to detect most of the priority measurements listed in Group II and III. The performance of existing in situ optical sensors today is limited. Of the Group II parameters, development of water velocity by laser velocimeters could be considered. Spectrographic techniques should be developed to identify Group III parameters. The spectrographic wavelength variability allows for multiple parameter detection using optical sensors.

Individual Sensor Applications/Characteristics--

Results of panel discussions on various individual sensors appear in outline form on the following pages, addressing them by measurement concept, as listed in the four categories described above.

Spectroradiometers (passive)
(General)

1. Applications
   Reflectance at various wavelengths.
   Inorganic sediment particles suspended in the air.

2. State of the Art
   a. Status
   b. Capabilities/Limitations
      Error limits not defined at this time; small size, weighs about 20-25 lbs; region (large area) oriented; used for fresh water but can be used for salt water, also easily adapted for use in water; limited by sunlight.
   c. Expertise/Source
      Dr. Frank Schiebe, U. S. Department of Agriculture.
      Dr. James Bailey, U. S. Navy, Office of Naval Research.
   d. Cost
      $2,500 off-the-shelf.

3. Short-Term (5-year) R & D Possibilities
   Once wavelength parameters are established, cost should decrease, many substances could be identified, i.e., algae, chlorophyll a.

Infrared Reflectance (Active/Passive Radiometer)

1. Applications
   Detects oil on water.

2. State of the Art
   a. Status
      Has been developed, presently attempting to manufacture for routine use.
   b. Capabilities/Limitations.
      Mounted above the water. Can be monostatic (transmitter and receiver side by side) or biostatic (transmitter and receiver mounted opposite each other across a body of water). In the biostatic receiver mode it scans (by a motor) the water, allowing examination of a broad expanse of water body. The method is 90% accurate, has proven very reliable. The two units are about 1 foot square, water and explosive proof, free from weather, require no servicing unless the pole they are mounted on changes the line of vision. Can scan 500-plus feet, two feet in diameter.
   c. Expertise/Sources
      Donald R. Jones, EPA, Washington, D.C.,
      Lt. William Plage, U. S. Coast Guard, Washington, D.C.,
      Wright & Wright, Inc., Massachusetts.

3. Short-Term (5-year) R & D Possibilities
   R & D complete at this time.
   Plan to use system, 5-10 units, in the ports of Baltimore and Houston in 1979 and 1980.

4. Remarks
   If this system is successful in the ports listed above then purchase by major oil companies is anticipated to give early alarm to prevent expensive spill cleanup costs due to late knowledge of spill.

Spectroradiometer (Active)
(General)

1. Applications
   a. Measurement of radiation reflected from a water surface at various optical wavelengths; energy source is provided internally. Measurements to be made remotely (reflectance) or underwater (back scattering).
   b. Inorganic and organic particles suspended in water, infrared from the optical measurements.

2. State of the Art
   a. Status
      (1) Oil detection - USCG work.
      (2) Other R & D unknown.
   b. Capabilities/Limitations
      Accuracy - good potential.
      Reliability - good potential.
      Size/Weight - could be developed in small package.
      Water Type - fresh/salt.
      Power Requirement - Could be considerable if CW is used. Strobe systems could reduce power consumption considerably.
      Serviceability - Should be no problem.
      Environmental Conditions - In air or underwater (fresh or saline).
      In air (-10° to 50°).
      Not affected by rain, wind, etc.
   c. Expertise/Sources
      No known research in direct subject. Manufacturing by ISCO, Texas Instruments, Rambie.
      Related research in passive spectroradiometry at USDA sedimentation laboratory (F. K. Schiebe and J. C. Ritchie).
   d. Cost
      Operational - None known in routine operation
      Capital - Could be quite low. Estimated less than $5000 for ultimate off-the-shelf instrument. Automation would add to cost.

3. Short-Term (5-year) Development Possibilities
   a. No known R & D for spectroradiometry.
      R & D at Texas Instruments for specific bands (IR).
      Product available from Rambie.
   b. Feasibility study needed to assess potential.

Fluorescene Spectrometer (Active)

1. Applications
   Chlorophyll a, oils, dissolved organics.

2. State of the Art
   a. Status
      Chlorophyll a - Routine application for continuous monitoring of strips in marine environments.
      Developmental system on NOAA buoy system for field testing.
      Development needed for fresh water application.
      Oil - Field-deployed buoy system for detection and identification.
      Total Organic Carbon (TOC) - Research.
      Algae species identification - Research.
   b. Capabilities/Limitations. Material identification based on excitation wavelength and/or fluoresced wavelength intensity measurement.
      Chlorophyll a (marine environment), 0-20 $mg/m^3 \pm 10\%$.
      Oil detection of presence on surface, coarse identification.
      TOC: Not established.
      Fouling of optical windows and components reduces reliability (cleaning cycle is a function of water condition).
      Chlorophyll a and oil detection system - ½ cubic feet and battery powered.
   c. Expertise/Sources. Chlorophyll a - Turner Designs, Mountain View, CA (modified for buoy use by Magnavox, Fort Wayne, Indiana).
      Oil - Spectrogram Corp., North Haven, Conn.
      TOC - Michael Bristow, EPA, Las Vegas.
      Algae Species Identification - Jack Hall, NASA, Langley.
   d. Cost.
      Chlorophyll a - $10K.
      Oil - $10K.

3. Short-Term (5-year) R & D Possibilities.
   R & D ongoing for chlorophyll a in fresh water, for TOC and algae species identification.
   R & D needed on anti-fouling devices or automated cleaning system - development needed on automated standardization and calibration systems.

4. Long-Term R & D Possibilities.
   R & D needed on discrimination of dissolved organics and oil types and quantity.

Active Light Transmission
(General)

1. Applications
   Light Attenuation Measurements; 90° scatter, forward scatter, differentiate between organic and inorganic particulate matter.

2. State of the Art
   a. Status
      Light attenuation and scatter - operational, some development.
      Forward scatter - developmental.
   b. Measurement of parameters of interest is dependent on the wavelength selection and angle of measurement. Accuracy, optical characteristics quite accurate but relating to parameters of interest is only fair; reliability is good; size and weight - light, compact, easily portable; Water type - all; serviceability - requires frequent service; environmental conditions - dependent on sensor or design.
   c. Expertise/Sources - Light attenuation by manufacturer. Forward Scatter - Jack Salzman, NASA-Lewis.
   d. Cost - Light attenuation and 90° scatter - $5K. Forward scatter unknown.

3. Short-Term (5-year) Development Possibilities
   Resolve fouling problems.
   Increase unattended operation capability.
   Make more automated.
   Redefine and standardize calibration and measurement units.

Transmissometer
(Active)

1. Applications
   Transmission of light through the water to determine trophic levels.

2. State of the Art
   a. Status
      Operational commercially available underwater use, operates continuously. Presently used on ocean buoys.
   b. Capabilities/Limitations
      Within 1% accuracy when first deployed. Life expectancy one month underwater due to fouling problem. Coating of sensor to retard organism fouling may be possible 20 lbs. (2' x 3" in diameter).
   c. Expertise/Sources
      Manufacturers - Hydro Products, MARTEK, KAHL, Inter-Ocean; Dr. Ed Michelena, NOAA, NSTL, Bay St. Louis, Missouri.
   d. Cost
      $3K off-the-shelf plus adaptation for NOAA use.

3. Short Term (5-year) R & D Possibilities
   R & D ongoing is to develop methods for reducing fouling. Another R & D need is for lower power consumption.

Refractometer (Active)

1. Applications
   Refractive index for salinity determinations

2. State of the Art
   a. Status
      Operational - commercially available hand-held model.
      Developmental - automatic recording.
   b. Capabilities/Limitations
      Accuracy ±.1% salinity for hand-held model.
      ±.2% for automatic recording model.
      If pollutant concentration is high, the accuracy will be degraded. Easy to clean.
      Limited to source of light.
   c. Expertise
      Mr. Edward Brainard, ENDECO, Marion, Massachusetts.
   d. Cost
      Hand-held model (which is the operational unit) - $1100. Recording type unit - $4500. Present recording scheme uses photographs of the viewing window.

3. Short-Term (5-year) R & D Possibilities
   Conversion to the use of a monochromatic light source. Will increase accuracy and allow 24-hour operation.

4. Long-Term R & D
   Develop sensor with an electronic digital output and also with an analog voltage output.

"Turbidity" Meter

1. Applications
   Measures light transmission and scattering through water to determine turbidity.

2. State of the Art
   a. Status
      Developed, being evaluated.
   b. Capabilities/Limitations
      Accuracy hard to define, probably better than 1%. Fresh water use but can be adapted for salt water. Window needs constant cleaning. Needs 110 V AC power; ½ cubic foot size. Needs weekly service and weather protection.
   c. Expertise/Sources
      James Ficken, U. S. Geological Survey, NSTL, Mississippi.
   d. Cost
      $20K for development: $2-5K for production.

3. Short-Term (5-year) R & D Possibilities
   Used as routine monitor short- and long-term. Production model could be completely automatic.

Microwave Instruments (General)
(Microwave Spectroscopy and Microwave Radar)

1. Applications
    - a. Microwave spectrum for specific identification of compounds.
    - b. Reflections from changes in dielectric constant in a bulk medium.

2. State of the Art
    - a. Status
      Present Application
        - Research into molecular structure and compound identification.
        - Measurement of water content of materials (soil, grain, snow, concrete, etc.) research stage only.
    - b. Capabilities/Limitations:
        - Highly specific but requires sample preparation identical to GC mass spectrometry, i.e., isolate compound in gas phase at low pressure.
        - Has not been applied to water monitoring.
        - Points to consider: accuracy, reliability, size/weight, water type, serviceability, environmental conditions.
    - c. Expertise Sources. At this state these instruments require highly skilled operators. There are no longer commercial sources of microwave spectrometers. Instruments are laboratory-assembled from purchased components. Sources are:
        - Microwave Spectroscopy - William Kirchoff, NBS
          Gaithersburg, MD.
        - Microwave Radar - Hal Boyne, NGS, Boulder, CO.
    - d. Cost:
      Microwave spectrometer cost is approximately $100K. Microwave radar instrument could be assembled for less than $10K. As there are no sensors in routine operational use, operational costs are not available, however, an instrument for measuring atmospheric formaldehyde based on microwave absorption has been used.

3. Short-Term (5-year) Development Possibilities
   Development of microwave spectroscopy as a routine analytical instrument is currently not being pursued. Packaging of data handling and development of a GC-microwave spectrometer interface is needed. A major drawback is the inability to identify a new substance if its spectrum is not already known. A major strength is specificity and capability of identifying components of gas phase mixtures. Quantification using isotopically-labeled spikes is also simple

since spectrums of different isotopes are distinct. Microwave radar has not yet been tested on water systems but has been tested on the materials listed above. Feasibility research would be useful.

Lidar Polarimeter (Active)

1. Applications
   Oil on water, concentrations of suspended solids.

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Detect oil on water and detect concentrations of solids in the water column; very accurate, depends on particle size distribution; not affected by sea state; scans an area; measurement can be adapted to in-water use with research; 24-hour operation; weather protected; serviceability depends on laser efficiency; weight of 50 pounds; 24 inches long, 4-inch diameter cylinder.
   c. Expertise/Sources
      Dr. Richard Newton, Texas A&M University.
   d. Cost
      $90K to date. Production cost indeterminate.

3. Short-Term (5-year) R & D possibilities
   Usefulness can be demonstrated in short-term with additional research.

Coherent Lidar Polarimeters (Active)

1. Applications

Concentrations of suspended solids, size distribution of suspended solids, presence of oil on a water surface, thickness of oil on the water surface, gross classification of oil type.

Measurement technique is to transmit narrowband polarized coherent light (laser) and measure the light backscattered from a water target in both polarization states. The measurement technique has been used as a non-contact measurement technique, but is applicable to a true in situ sensor.

2. State of the Art

a. Status

The measurement concept has been demonstrated both analytically and experimentally. An automated non-contact single wavelength sensor has been built to demonstrate detection of oil on water and the capability to measure concentrations of suspended solids. A dual wavelength laboratory system has been built and used to demonstrate the capability of oil thickness determination and gross oil classification. The status of the sensor concept would be considered developmental.

[illegible]. Capabilities/Limitations

The ratio of the "cross" polarized backscatter to the "like" polarized backscatter (termed depolarization ratio) is related to the concentration of suspended solids in the water volume. This relationship is independent of surface characteristics of the water when the instrument is operated in a non-contact mode. The depolarization ratio is not only dependent on concentration of suspended solids, but also on the size distribution of these solids. As a result, by using a multiple wavelength light source, measurement of particle size distribution is conceivable. In addition, in the in situ mode the instrument could be used to profile concentrations of suspended solids within a water volume by lowering the sensor through the water or by pumping water from different levels to the sensor.

In the non-contact mode (sensor above the water), the presence of surface contaminants such as oil can be detected by the magnitude of the like or cross polarized backscatter measurements at a single wavelength. Two or more wavelengths add the capability of oil thickness determination and oil classification.

Serviceability and reliability depend primarily upon the lasers utilized. The remainder of electronics required should be highly reliable.

c. Expertise/Sources
   Dr. Richard Newton, Texas A & M University
   Dr. John Rouse, University of Missouri

d. Cost
   Production cost indeterminate at this time.

3. Short- and Long-Term Developmental Possibilities
   a. Research and development is currently not being pursued by any Federal agency either in-house or by outside funding.
   b. Development needs include:
      (1) Investigation of effect of organic materials.
      (2) Investigation to determine ability to profile suspended solid concentrations.
      (3) Investigation of ability to determine particle size distribution.
      (4) Investigation into ability of Raman scattering for foreign substance identification.

ELECTROCHEMICAL SENSOR TECHNOLOGY: Working Panel Report

Members:

Richard A. Durst, NBS, Chairman
Roger G. Bates, University of Florida
Walter J. Blaedel, University of Wisconsin
Chung-Chiun Liu, University of Pittsburgh
J. Anthony Llewellyn, University of South Florida
Gary Ward, NOAA
Judd R. Wilkins, NASA

Summary

The work of this panel was hampered by two deficiencies: time and user expertise. Without the first-hand knowledge of sensor users on the panel, it was difficult in many cases to thoroughly address the types of problems encountered in real-world monitoring situations. Most of the panel participants were laboratory scientists having little experience with the problems of field measurements. Future panels of this type should have the representation of users with diverse monitoring experience.

Because of the lack of time, all parameters which are amenable to electrochemical sensor monitoring were not discussed and should be addressed at some future workshop. The parameters which were not discussed included alkalinity, oxygen demand, calcium, boron, carbon dioxide and carbonates, total organic mercury, nickel, potassium, sodium, nitrate and nitrite, urea, amino acids, redox, and ATP.

The Electrochemical Sensor Technology Working Panel divided its discussions into two primary areas, amperometric and potentiometric sensors. The amperometric sensors are a very valuable and versatile technique for evaluating water parameters. They are useful with analytical techniques as detectors for liquid chromatography, and in titration procedures, and have a great potential for organic analysis. The operational mode determines the response time. This technology is capable of detecting electroactive substances such as: organic compounds, metals, halides, synthetic organic compounds, oxygen and chlorine, and oxygen demand. The potentiometric sensors are small and inexpensive, and can be easily adapted to automated in situ monitoring applications. They will normally require sample pretreatment, but yield good accuracy with frequent calibration. Capabilities exist for detecting selected cations and anions, including fluorides, chloride, cyanide, sulfide, calcium, coppers, cadmium, and potassium, coliform bacteria, and redox.

A summary of discussions of sensors in the amperometric category follows:

Sensor Type--
    Amperometric (Summary)

Measurement Applications--
    Electroactive substances:
        Metals
        Organic Compounds
        Halides
        Synthetic Organic Compounds
        Oxygen and Chlorine
        Oxygen Demand

Advantages--

High sensitivity; economical; wide applicability - any electroactive substance (direct or indirect); simplicity - potentially portable for on-site applications (can be miniaturized and amenable to battery operation); usable in all types of water; amenable to a variety of operational modes including amperometric titrations, differential pulse polarography, anodic stripping voltammetry, cyclic voltammetry, and chromatographic detectors. When operated in the steady-state mode, the response is rapid.

Disadvantages--

Poor selectivity and interferences when used without sample preparation. Electrodes will require periodic cleaning.

Near-Term R & D Recommendations--

Development of amperometric methods for providing specific redox information; investigation of oxidation-reduction potential has a descriptive parameter for characterizing the redox strength of water systems. Development of automated systems for on-site monitoring.

Remarks and Conclusions--

Amperometric sensors are very valuable and versatile techniques for the evaluation of many water parameters. High capabilities for automated on-site measurements. Useful in conjunction with other techniques, for example, as detectors for liquid chromatography and in titration procedures. Great potential for organic analysis. Operational mode determines the response time.

Summary remarks regarding potentiometric sensors included the following:

Sensor Type--
    Potentiometric (Summary)

Measurement Applications--

Selected cations and anions, including fluoride, chloride, cyanide, sulfide, calcium, copper, cadmium, lead, potassium, and sodium, and water hardness. Gases, including carbon dioxide, ammonia, oxygen, sulfur dioxide, nitrogen oxides, and hydrogen sulfide. Enzymes and substrates; coliform bacteria; pH; redox (unsatisfactory).

Advantages--

Inexpensive; simple mode of operation; sensitivity suitable for many monitoring applications; easily automated; good selectivity with proper sample preparation; small size; adequate response time for many applications; can be modified in various ways for gas, biochemical and microbiological measurements; portable; useable in all water types with sample preparation; useful for both direct and indirect measurements; rugged; good accuracy with frequent calibration and control of operating conditions.

Disadvantages--

Selectivity normally requires sample pretreatment; long-term instability; susceptible to fouling; temperature sensitivity; liquid junction problems with reference electrodes.

Near-Term R & D Recommendations--

Devise methods for the elimination of liquid junction problems. Improve methods for prevention or removal of fouling. Development of better automated pretreatment methods. Selected enzyme electrode development. Development of microbiological sensors; development of automated on-site systems for ion-selective electrodes. Miniaturization.

Long-Term R & D Recommendations--

Major program in enzyme electrode research. Research and development into new membrane technologies and ion-sensitive field-effect transistors.

Remarks and Conclusions--

Should be easily adaptable to automated on-site monitoring applications for continuous real-time analysis. Susceptible to a variety of interferences and normally will require sample pretreatment. Versatile for both direct and indirect measurements. Membrane fouling and long-term instability are problems which must be overcome. Response time needs improvement. Present potentiometric redox methods are unsuitable and new technology should be developed.

The Panel's review of various individual sensors is reported in the following outlines, which cover these parameters:

Glass electrode
pH

ion selective electrode
- sulfide ion
- chloride ion
- fluoride ion
- heavy metals (copper, cadmium, lead and silver)

gas-sensing electrodes
- ammonia
- hydrogen sulfide
- carbon dioxide
- sulfur dioxide
- nitrogen oxides

redox hydrogen electrode
- coliform bacteria

amperometric
- heavy metals (copper, cadmium, lead, zinc)

amperometric, galvanic, chronocoulometric
- dissolved oxygen

electrochemical
- conductivity

Potentiometric (glass-electrode)

1. Applications
   pH

2. State of the Art
   a. Status
      Operational
   b. Capabilities/Limitations
      The accuracy and precision is sufficient for most applications when the electrode is functioning properly but in practice may not be achievable. The size and weight are not problems. There are no interferences in natural waters. The sensor requires a calibration frequency commensurate with the accuracy needed. The electrode is sensitive to electrical noise and is fragile.
   c. Expertise/Sources
      Roger G. Bates, University of Florida; Beckman Instruments; and Corning.
   d. Cost
      $50-$400

3. Short-Term (5-year) Development Possibilities
   R & D ongoing or programmed - No information.
   R & D needs and gaps - Prevention of fouling, calibration methods and high-pressure studies.

4. Long-Term Development Possibilities
   R & D ongoing or programmed - No information.
   R & D needs and gaps - The development of a pH sensor based on a new technology but of low priority compared to other sensor needs.

Potentiometric (ion-selective electrode)

1. Applications
   Sulfide ion

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Susceptible to interferences and equilibria between chemical forms. Usually requires pretreatment; pH control is important. Poisoning of membrane by mercury. Good stability.
   c. Expertise
      James Ross, Orion Research
   d. Cost
      $250-$500

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - No information
   b. R & D needs and gaps - Development for deep ocean measurements required.

Potentiometric (ion-selective electrode)

1. Applications
   Fluoride ion

2. State of the Art
   a. Status
      Operational
   b. Capabilities/Limitations
      The sensitivity is sufficient for most applications. It is useable in all types of natural waters, but may require pretreatment in certain cases. It has good stability, has a precision better than 5 percent, and 95 percent response in less than two minutes.
   c. Expertise/Sources
      James Ross, Orion Research; Martin Frant, Foxboro Company.
   d. Cost
      $250-$600

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - Development of pretreatment procedures for special applications.

Potentiometric (ion-selective electrode)

1. Applications
   Chloride ion

2. State of the Art
   a. Status
      Operational
   b. Capabilities/Limitations
      Rugged; useable in all types of water (requires pretreatment in effluent monitoring); fast response; good stability and sufficient sensitivity.
   c. Expertise/Sources
      Orion Research and Hydrolab
   d. Cost
      $250-$600

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - The development of sample pretreatment methods for effluent monitoring.

Potentiometric (ion-selective electrodes)

1. Applications
   Heavy metals (copper, cadmium, lead, and silver)

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Sensitivity is borderline for natural ambient levels; precision is approximately 5-10 percent. Useable in all water types but pretreatment necessary by ionic strength adjustment and masking of interferences. Electrodes require frequent calibration and reconditioning.
   c. Expertise/Sources
      James Ross, Orion Research
   d. Cost
      $250-$600.

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - Research and development ongoing.
   b. R & D needs and gaps - Presently not as sensitive as voltammetric devices but may be improved by new membrane materials and the development of pretreatment techniques.

Potentiometric (gas-sensing electrodes)

1. Applications
   Ammonia, hydrogen sulfide, carbon dioxide, sulfur dioxide and nitrogen oxides.

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Sufficient sensitivity; slow response time. Reference solution requires periodic replacement; pretreatment of sample usually needed; susceptible to membrane fouling.
   c. Expertise
      James Ross, Orion Research
   d. Cost
      $300-$500

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - Systems development for monitoring, including pretreatment of the sample.
   b. R & D needs and gaps - Development of electrodes for other gases than those indicated above.

Potentiometric (redox hydrogen electrode)

1. Applications
   Coliform bacteria

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Freedom from interferences; requires monthly calibration; does not function in high salt solutions; response time is a function of the number of cells and rate of division.
   c. Expertise/Sources
      Judd Wilkins, NASA; C. C. Liu, University of Pittsburgh.
   d. Cost
      $10-$200.

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - Development of electrode configurations and flow systems.
   b. R & D needs and gaps - Fundamental studies of electrochemical mechanisms and biochemical reactions.

4. Long-Term Development Possiblities
   a. R & D ongoing or programmed - Investigate possibilities of using similar systems to monitor other microorganisms.

Amperometric

1. Applications
   Heavy metals (copper, cadmium, lead, and zinc).

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Sensitivity is sufficient for most monitoring applications. Not automated; sample preparation required; good capability for on-site automation; stability not high; application to all water types with pretreatment; accuracy and precision not high but could be improved.
   c. Expertise/Sources
      Walter Blaedel, University of Wisconsin; Judd Flato, PAR; Tom Hoover, EPA, Athens; Ray Clem, Lawrence Berkeley Laboratory; Al Zirino, Naval Undersea Research Center; W. Davison and M. Whitfield, reference: Journal Electroanalytical Chemistry, 75, 763 (1977).
   d. Cost
      Inexpensive (potentially disposable).

3. Short-Term Development Possiblities
   a. R & D ongoing or programmed - Seek new applications for available systems and development of new electrode designs.
   b. R & D needs and gaps - Engineering research and development of systems packages for on-site monitoring.

Electrochemical
(amperometric, galvanic and chronocoulometric)

1. Applications
   Dissolved oxygen

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Membrane instability and fouling; requires sample around sensor to be continuously renewed, except for pulsed operations; sensitivity is sufficient; accuracy and precision depend on calibration procedure. Interferences - chlorine and hydrogen sulfide and possibly volatile organic sulfides. Required calibration frequency unsuitable for long-term monitoring. Response time is too slow for profiling. Useable in all water types (except for specific interferences).
   c. Expertise/Sources
      K. H. Mancy, University of Michigan; J. A. Llewellyn, University of South Florida; G. Ward, NOAA; C. C. Liu, University of Pittsburgh; Yellow Springs Instrument Company; Beckman Instruments; Orbisphere; Martek.
   d. Cost
      $100-$200 ($1000 for high-pressure sensor)

3. Short Term Development Possibilities
   a. R & D ongoing or programmed - Considerable R & D in progress.
   b. R & D needs and gaps - Studies into membrane properties; improvement of stability.

Electrochemical

1. Applications
   Conductivity

2. State of the Art
   a. Status
      Operational
   b. Capabilities/Limitations
      Sufficient accuracy and sensitivity; calibration frequency about two - three days in salt water; useable in all types of water; response decreases with decreasing temperature; may require filtration of sample; nonspecific response.
   c. Expertise/Sources
      James Sprenke, NOAA
   d. Cost
      Less than $500

3. Short-Term Development Possibilities
   a. R & D ongoing or programmed - Improvement of precision.
   b. R & D needs and gaps - Miniaturization and improvement in stability.

4. Long-Term Development Possibilities
   a. R & D ongoing or programmed - Research into the improvement of the correlation between conductivity and salinity.

ELECTROPHYSICAL SENSOR TECHNOLOGY: Working Panel Report

Members

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Summary

Some of the most powerful tools discussed by this panel include acoustical and radioactive methods. The acoustical methods can provide information on the thickness of oil and hazardous materials (e.g., densities less than water), and sedimentation concentration. Acoustical methods (passive) can provide information on activities of marine life, such as snapper shrimp and schools of croakers. Radioactive techniques include the use of neutron activation and energy dispersive X-rays for measurement of heavy metals. Electromechanical methods included the use of rotors and floats for measuring water velocity and tides. It was emphasized that macroscopic measurements are often overlooked, but are essential to understand the large picture such as total stream flow and oil coverage. For example, rather than measuring flow velocity in a stream or area, acoustical devices could be used to measure the average velocity over a much longer path distance.

It was noted that the advent of the microcomputer devices incorporated in the sensor package will considerably reduce the need for expertise in the operation of these systems. This coupled with new technology such as solid state devices (thermistor circuits) for detecting thin films of oil and other pollutants shows great promise. Additionally, packaging and the auxiliary devices required to keep sensors in operation should not be neglected. It must also be remembered that most sensor systems will operate much more satisfactorily if they have anti-fouling and cleaning devices attached to them.

Sensor Technology

Five types of electrophysical sensors were discussed in detail by the Working Panel. These were:

- acoustical
- electrical

- electromechanical
- differential pressure
- radioactivity

A summary of these discussions is provided in the following outlines.

Acoustical

1. Definition of Technology
   Involves measurements of sound transport and characteristics which are peculiar to parameters of interest.

2. Applications
   Parameters such as depth, profiling, velocity, direction, density, oil concentration are important applications.

3. Advantages
   These methods cover a wide range of applicability.

4. Disadvantages
   Probably the main disadvantage at this time is the cost of these systems, but indications are that significant progress is being made in this area of cost reduction.

5. Near-Term R & D Recommendations
   The need for increased application to sediment concentration by acoustical scatter, using such things as cavity resonance, frequency slewing.

6. Long-Term R & D Recommendations
   Doppler shift velocity profiling in swift water environments and the use of acoustics in measuring water velocities of low values (0-10 cm/sec).

7. Remarks and Conclusions
   Many sophisticated acoustical devices developed by military and space research can be selectively applied to water quality sensing. Even considering the complexity and cost, the advent of microprocessors improves the capability for acoustical measurements.

Electrical

1. Definition of Technology
   Involves the measurement of resistance, resistivity, and voltage as the result of physical change. This can be associated with two basic applications--the measurement of temperature and the measurement of specific conductance. In the measurement of temperature various elements, including RTD's and/or thermistors and thermocouples are used. Conductance systems utilize inductive and resistive techniques.

2. Applications
   Temperature and specific electrical conductance, which is related to salinity and dissolved solids.

3. Advantages
   Temperature elements are developed and commercially available for most applications. The conductivity measurements are fairly well defined for salt water and have recently been applied to fresh water.

4. Disadvantages
   None identified for temperature. Conductance sensor configurations are not as small as desired for some requirements.

5. Near-Term R & D Recommendations
   No specific recommendations for temperature sensors other than those needed for special applications are necessary. For conductivity, more improvement is needed in reducing the affects of fouling and in reducing the size of inductive cells.

6. Long-Term R & D Recommendations
   None identified

7. Remarks & Conclusions
   The methods for measuring temperature seem to be as far advanced as necessary for most monitoring applications. Much work has been done in the specific conductance measurements and we have considerable expertise represented throughout the country. The relationship of conductance to salinity in salt water is well defined. It is not well defined in fresh water. The measurement can be used as a secondary input to correct other measurements such as correcting the concentration of a dissolved oxygen probe.

Electromechanical

1. Definition of Technology
   Depth measurements include physical sounding, floats, gages, and staffs. Flow measurements include drag devices, tracers, rotors, and vanes. Density measurements include vibrating tubes.

2. Applications
   Depth and flow.

3. Advantages
   Most of these parameters are measured by devices that are fairly inexpensive, easily operated and in most cases durable. However, in long submergence in water, quite a few are subject to fouling.

4. Disadvantages
   Disadvantages associated with mechanical devices are that they usually require some type of fixed installation and that generation of an electrical signal usually requires other transducers or devices.

5. Near-Term R & D Recommendations
   Could be replaced by more advanced methods, e.g. acoustics.

6. Long-Term R & D Recommendations
   Some of the mechanical methods are still quite good if more work is done to repackage and provide protection from fouling.

7. Remarks & Conclusions
   These methods are used quite frequently. Thousands of stations are located throughout the country and will continue to be used in the future. Some of the simple mechanical methods cannot be discounted.

Differential Pressure

1. Definition of Technology
   New generation pressure transducers of the quartz crystal type exhibit changes in resonant frequency with variation in pressure. Direct digital outputs are possible.

2. Applications
   Density and determination of size and concentration of suspended sediment in a settling water column.

3. Advantages
   Relatively non-fouling methods for measuring density, water stage and wave height and relating these to total suspended solids. Can replace expensive float structures. Many devices available.

4. Disadvantages
   Relative high cost for accurate stable sensor.

5. Near-Term R & D Recommendations
   Efforts should be made to reduce the cost of accurate, stable sensors.

6. Long-Term R & D Recommendations
   The use of differential pressure methods in determinating sediment concentration and size distribution.

7. Remarks & Conclusions
   The use of differential pressure can be applied to the measurement of density which could be related to salinity and suspended solids. The method can also be applied to the measurement of velocity and flow.

Radioactivity

1. Definition of Technology
   Includes ionization detectors, scintillation counters, and semiconductor devices.

2. Applications
   Measurement of radioactive materials through the identification of radionuclide and type of radiation. There may be some application for density and suspended sediment measurement.

3. Advantages
   High precision and accuracy for some applications. Fairly low cost, reliable.

4. Disadvantages
   For some applications, may require preconcentration.

5. Near-Term R & D Recommendations
   This working panel felt the need for more inputs from experts in the field. Much of the development has probably already been completed. The application of this technology to suspended sediment measurement should be explored.

6. Long-Term R & D Recommendations
   None

7. Remarks & Conclusions
   These methods show great promise and are being used in field measurements of the above parameters.

AUTOMATED WET CHEMICAL SENSOR TECHNOLOGY: Working Panel Report

Members

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Summary

A number of sensor technologies that could be used individually or in combination with automated pretreatment systesm were considered. These include ultraviolet and colorimetric detection techniques, membrane electrodes and specific ion electrodes. These would present signal processing problems for complete automation, but most are resolvable with microprocessors.

A certain amount of pretreatment will always be necessary. Though a high capital cost can be expected initially, a very large number of water quality parameters lend themselves to detection and quantification by this technology. Automatic cleaning would be necessary, often, depending upon types of waters. It is expected that automatic measurements can be extended from the present capability of a few hours to a few hundred hours by application of available technology. Measurements of total dissolved phosphorus, nitrogen compounds, and dissolved total organic carbon should be pursued.

Automated wet chemistry is the automation of on-line sample pretreatment for detection of parameters by sensor systems. It involves elimination of substances that would interfere with detection and requires minimum attention and maintenance so that it is applicable for field use (Figure 1). The sensor and package should operate unattended in, on, or immediately adjacent to the water body being monitored, and at the field location where the measurement is desired, as opposed to a laboratory facility, either fixed or mobile.

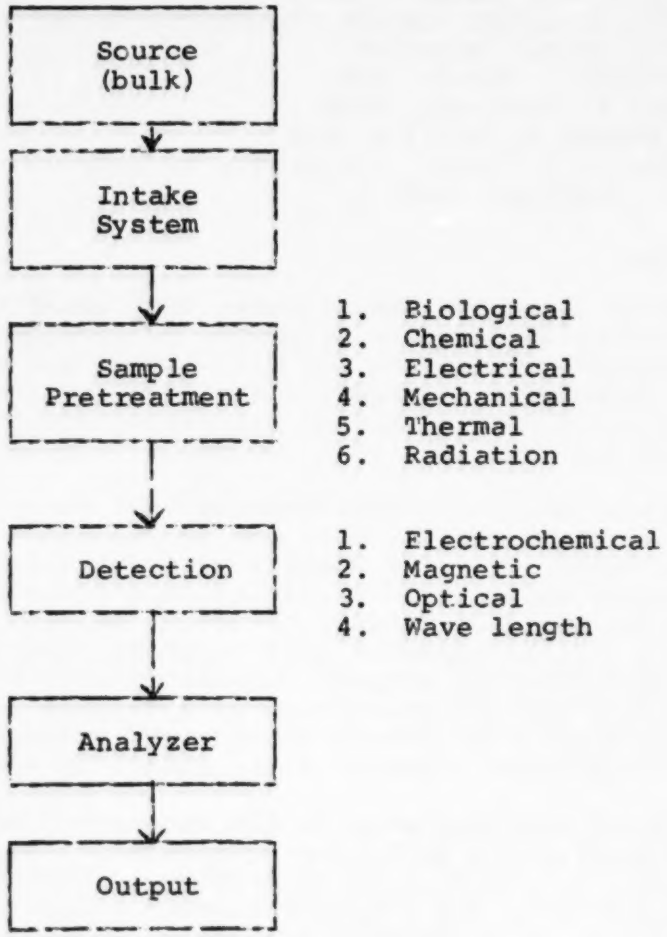
Source (bulk)
Intake System
Sample Pretreatment
1. Biological
2. Chemical
3. Electrical
4. Mechanical
5. Thermal
6. Radiation
Detection
1. Electrochemical
2. Magnetic
3. Optical
4. Wave length
Analyzer
Output

Figure 1. Automated Wet Chemistry Technology

A summary of sensor technology follows:

Applications (Water Type)--

a.	reservoir	g.	portable water supplies
b.	rivers	h.	rainfall
c.	lakes	i.	oceans
d.	estuaries	j.	reclaimed waters
e.	groundwater	k.	dredged material waters
f.	wastewater		

Advantages--
- Ability to measure:
  a. Expands the capability of a specific sensor type and minimizes effects of interferences and environmental factors.
  b. Allows concurrent multiple parameter analysis.
  c. Provides ability to measure large number of samples.
- Precision:
  a. Permits reduction of operator-induced error.
  b. Amenable to automated calibration and operation under computer control in or near real time.
- Frequency:
  a. Provides a high production rate.
- Cost:
  a. Cost effective.
  b. Provides flexibility of application.
  c. Requires minimum maintenance.

Disadvantages--
- Capital cost can be high.
- Operator skill requirements are high.
- System packages can be highly complex.

Near-Term R & D Recommendations--
- Development of miniaturized modular packaging for in situ and on site field installation.
- Assess performance characteristics and cost effectiveness.
- Design modules amenable to microprocessor control.
- Develop combination of wet chemistry modules tailored to meet needs associated with specific classes of water.
- Develop new wet chemistry methods for various water quality parameter in different classes of water.
- Expand, demonstrate, and improvement of available methodologies.

Long-Term R & D Recommendation--
- Continued emphass on all the items identified as short range R & D goals.
- Increased emphasis on:
  a. Miniaturization
  b. Remote operation capability

c. Product reliability
Continued search for new technology within related field of research.

Remarks and Recommendations--

Automated wet chemical procedures lend themselves to the detection and quantifying of a large number of water quality parameters. The main challenge is the adaptation of these measurement techniques to field applications. Without sample pretreatment, a large number of sensor systems cannot be applied to water quality surveillance and monitoring. Another important aspect of unattended field installation of wet chemistry methodology for water quality analysis is automatic cleaning. In system design and packaging, procedures for determining the type of cleaning (chemical, electrical, mechanical) required for the various water classes need to address such variables as frequency, time, chemical constituents and specified conditions as functions of the plumbing and detection components.

The Working Panel believes that the terminology for identifying water quality parameters of concern to the various agencies should conform to conventional analytical chemistry. Such parameters as available nitrogen and dissolved phosphorus, if used, should be defined. Our suggestion is to use ortho and polyphosphate and total nitrogen, TN soluble nitrogen (free NH_4, NO_3, NO_2) and unsoluble nitrogen (particulate) to define what is meant by phosphorus and nitrogen.

It is recommended that interdisciplinary research and investigations with the biological and medical disciplines be initiated with the objective of developing new sensing techniques.

Some of the sensor types, particularly the ultraviolet, colorimetric and electrochemical types could be developed for completely submersible in situ systems for deployment near shore or on buoys. Much of the basic technology for designing and controlling underwater electromechanical apparatus has been developed in oceanography and processes control.

Individual Sensor Applications/Characteristics--

Automated Wet Chemistry Technology Work Panel discussions of specific sensors were broken down to address four types:

- colorimetric
- electrochemical
- on-line ultraviolet absorption
- energy dispersive x-ray

Sensor Technology

The Panel comments on individual sensors are summarized in the following outlines.

Colorometric

1. Applications
   Total N, NO_3, NH_4, Kjeldahl N, Ortho P, Cl, COD, Total P and others.

2. State of the Art
   a. Status
      Developmental
   b. Capabilities/Limitations
      Accuracy and reliability-variable, tempermental;
      Operational longevity-2-hr life at present, 1 week is needed for unattended life;
      Suspended solids will need to be controlled in water;
      Precision-not accurate;
      Water type applications (see water type classification in summary, item 2)
         high probability of measurement - types a, c, e, g, h, j.
         medium probability of measurement - types d, i.
         low probability of measurement - types b, f, k.
      Serviceability-requires highly qualified individual;
      Environmental conditions-enclosed (no freezing or sunlight).
   c. Expertise/Sources
      Federal, commercial, university, and clinical.
   d. Cost
      For sensors in routine operation:
         Developmental - \$250K
         Capital - \$15K
         Operations and maintenance - \$30K (annually)

3. Short-Term (5-year) Development Possibilities
   a. R & D ongoing or programmed - not presently known.
   b. R & D needs and gaps - automation, packaging for field application.

4. Long-Term Development Possibilities
   a. R & D ongoing or programmed - not needed for engineering needs.
   b. R & D needs and gaps - not needed for engineering needs.

Electrochemical

1. Applications
   NH_4, NO_3-N, residual chlorine, ozone; trace metals, alkalies, alkali earth metals, florides, cyanide and other electrochemically detectable species where some pretreatment is needed.

2. State of the Art
   - a. Status
     Research, Developmental, Operational
     Sensors are available for the measurement of parameters shown in each of the measurement categories.
   - b. Capabilities/Limitations:
     Accuracy-precision varies with the sensor;
     Size/weight-portable;
     Water type applications (all in summary list, item 2)
     Serviceability-varies with the type of sensor on a hourly, daily, weekly basis;
     Environmental conditions-can withstand many types of environmental stresses, does not require large quantities of water.
   - c. Expertise/Sources
     Federal, university, commercial, and clinical
   - d. Cost
     For sensors in routine operation: $500 - $2000 per package.

3. Short-Term (5-year) Development Possibilities
   - a. R & D ongoing or programmed - some are demonstrated under field conditions.
   - b. R & D needs and gaps - for process control in treatment plant in situ conditions.

4. Long-Term Development Possibilities
   - a. R & D ongoing or programmed - Technology needs to be accomplished for unattended, reliable, low cost packaging for field and in situ use.
   - b. R & D needs and gaps - None identified.

On-line Ultraviolet Absorption

1. Applications
   Unsaturated resonating organic compounds, phenolic groups, pesticides, etc.

2. State of the Art
   a. Status
      Developmental - Limited to effluents where normal consituents are known.
   b. Capabilities/Limitations
      Reliability-good with further development;
      Size/weight-small
      Water type applications-clear water;
      Serviceability - unknown (expected to be good);
      Environmental conditions - no housing can be put in the field.
   c. Expertise/Sources
      Federal, commercial, university and clinical.
   d. Cost
      For sensors in routine operation:
      (1) $5K per package
      (2) Operation and maintenance - unknown

3. Short-Term (5-year) Development Possibilities
   a. R & D ongoing or programmed - Investigation of field applications to difficult types of water. Non-specificity - can only detect organics which absorb in that specific light wavelength.
   b. R & D needs and gaps - None identified

4. Long-Term Development Possibilities
   a. R & D ongoing or programmed - Investigate field applications for difference types of waters.
   b. R & D needs and gaps - in situ measurement.

Energy Dispersive X-ray

1. Applications

   All heavy metals with the exception of the metal used for the X-ray window.

2. State of the Art
   - a. Status

     Developmental routine: Detection ability - ppb range at low end and at upper end. Filter paper saturation problems exist because of matrix interference and very high metalic ion concentrations.
   - b. Capabilities/Limitations

     Reliability-unknown but expected to be within design expectations over a target period of 30-day unattended operation;
     Size/weight-13 cu ft, 420 lbs.
     Water type applications-all except dredged sediment;
     Serviceability-unknown;
     Environmental conditions - no freezing temperatures, etc.
   - c. Expertise/Sources

     Industry, Federal, university, and clinical
     A. F. Mentink, EPA, EMSL-Cincinnati
   - d. Cost

     Development and demonstration - $500K. For sensors in routine operation - $50K for a production package.
     Operations and maintenance - $20K annually/station

3. Short-Term (5-year) Development Possibilities
   - a. R & D ongoing or programmed - Development of additional filter papers and the associated resins.
   - b. R & D needs and gaps - Greater portability.

4. Long-Term Development Possibilities
   - a. R & D ongoing or programmed - Testing to be completed under 3-a.
   - b. R & D needs and gaps - Completely automated remote installation.

NEEDS AND TECHNOLOGY INTEGRATION: Working Panel Report

Members

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Summary

It was the unanimous consensus of the agency representatives attending the workshop that there is indeed a great need for development of automated in situ measurement systems[1] to satisfy requirements for aquisition of water quality information. It was noted that because such sensors do not exist, our ability to collect the nationwide field information necessary for adequate resource management and protection is seriously limited. Also noted was the fact that because these sensors are not available, development of more advanced measurement systems such as satellite and aircraft remote sensing is also limited as adequate means for obtaining supportive ground truth information do not exist.

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[1] Automated in situ measurement systems for the purpose of this workshop were defined to be sensors or sensor systems that operate in contact or near contact with the water they are measuring; they must operate unattended in, on, or immediately adjacent to the water body being monitored, and at the field location where the measurement is desired versus a laboratory facility. A sensor system may consist of several elements which are used to pre-condition the sample as in the case of automated wet chemistry, with the overall system producing a signal that is proportional to the parameter being measured.

It was recognized that natural waters, composed of groundwater, streams, rivers, lakes, estuaries and the oceans, are keys to survival because of both the benefits they provide and the disaster they may carry. Water as drinking water and for agricultural purposes is vital to existence. It plays a key role in the removal of wastes, the production of energy and the establishment of climate. It is also of significant importance for its ability to distribute pollutants and hazardous materials throughout the environment, contaminating drinking water, food supplies and recreational facilities. It is important therefore, that we both understand and manage our water resources effectively, not only from the standpoint of conservation, but also from the perspective of public health and safety.

The aquisition of adequate reliable water data is the first step in any water management program, whether the objectives are conservation oriented or scientific in nature, i.e., for the allocation of water resources or for the understanding of the mechanisms and pathways of pollutants.

Data must be collected frequently, sometimes continuously, in remote locations, under adverse environments and often over very large areas. Practice at the present time is to send people into the field to collect samples for analysis or to perform the frequent maintenance required for the few automatic instruments that are available. Such practice provides neither the real time information that is required in many cases, nor the adequate quantity and quality of data required for proper management.

It was acknowledged by workshop participants that present capabilities for data transmission, storage, retrieval and manipulation far exceed capabilities to make accurate, reliable real-time measurement of necessary water quality variables.

It was concluded that automatic sensor systems would have wide application for water quality monitoring by many agencies in fresh water streams and lakes, in groundwater and in the marine waters of the ocean and coastal zones. For this reason, it was strongly recommended that agencies cooperate as much as possible to develop these automated in situ systems for their mutual benefit through joint interagency research and development efforts.

Although agencies require water quality measurements for different purposes and in different environments, it was noted that there are many areas where requirements overlap. Areas of mutual interest regarding high priority measurements were identified and grouped into three categories according to degree of commonality. These are detailed in the Measurement Needs Working Panel report. Group 1 parameters were found to be of high priority and great interest to most agencies with water measurement programs. Group 2 parameters were of high priority interest to many agencies, and Group 3 parameters were of high priority but specialized interest to a few agencies. For example, the monitoring of toxic substances is extremely important, however, EPA and the U. S. Coast Guard are the agencies with primary concern for such measurements. On the other hand, suspended particulate measurements are of high priority concern to all agencies since such information is necessary for the quantification of sediment transport (U. S. Department of Agriculture, U. S. Geological Survey, U. S. Army Corps of Engineers) as well as the study of pollution transport mechanisms (EPA, NOAA, Department of Energy) and ground truth support for remotely sensed phenomena (NASA).

All agencies represented at the workshop, with the exception of NASA, had active water measurement programs and could therefore contribute to the discussion of measurement requirements. NASA was recognized, however, to have a substantial interest in development of water measurement technology since NASA is anxious to promote application to national problems through the considerable technical expertise it has acquired through the space program. Furthermore, NASA has a budget to facilitate such technology transfer.

Findings and Recommendations

1. Although the Measurement Needs Working Panel was able to identify high priority measurements required by most agencies, it was felt that definition of requirements specific enough for design and development of measurement systems related to various application areas could not be generalized in terms of overall agency requirements by the relatively small number or panel members present. A preliminary summary of agency needs is included in Measurement Needs Panel report. The panel prepared a series of questions to be answered regarding specific requirements.

It is Recommended that:

(a) "Requirements Survey" be formally conducted within each agency to reflect overall agency needs and that results of this national inventory be published by a workshop follow-up committee.

2. It was recognized that this workshop was the first meeting of an interagency group for discussion of common needs and requirements for automated water quality measurement technology. General agreement existed on the value of continuing such dialogue in order to establish national priorities,

accelerate technological development and coordinate agency efforts to minimize duplication. Although little duplication could be identified except in a few specialized areas of hydrology, the need for better interagency coordination was recognized. It was felt that improved communication would lead to better coordination and more efficient application of the always limited budgetary resources.

It is Recommended that:

(a) more sensor development be carried out through interagency cooperative efforts utilizing the considerable expertise that already exists in the Federal system.

(b) a similar workshop be held approximately six months after the report of this workshop is issued and that coverage be expanded to include areas that were inadequately covered (biology and radioactivity) at this workshop.

(c) a steering committee be formed to follow through on the action items of this workshop and to plan future coordination.

(d) efforts be made to interest one or more of the professional societies (e.g. IEEE, ISA, etc.) in including sessions devoted to automated in situ sensor development for water quality measurement in their future conference plans.

3. It was noted that the research and development capabilities of private industry are considerable and if a profitable market could be identified, private industry would be willing t use its own resources to develop many of the devices needed for automated in situ measurement.

It is Recommended that:

(a) an interagency briefing on the results of this workshop be delivered to interested industry representatives after the workshop report has been completed.

4. The technology exists at the present time to develop many of the automated in situ sensors with real time data collection capabilities required for Federal agency programs. With minimum effort, short term development could yield automated sensors to meet some of the interagency requirements that have been identified. Additionally, interim stages of development will frequently result in a number of automated devices for immediate use in the laboratory. Such intermediate development stages will provide useful laboratory devices that can reduce manpower requirements as well as the human variability inherent in manual sampling and analytical methods. Since little funding has been directed toward such development to data, inadequate programming to focus on this area has resulted.

It is Recommended that:

(a) agencies assume lead roles in the development of indicated sensors as outlined in Table 1 on page 10, pursuing additional funding and support in-house and through cooperative arrangements with other interested agencies to support research and development efforts.

(b) the technological expertise of NASA be applied to address the need for imporved sensors through the technology transfer program, as it is apparent that NASA could make substantial contributions in this area.

5. One of the areas that has been specifically identified as having a high potential for short term development success is automated wet chemistry. For many of the "Group 2," parameters cited by the Measurement Needs Panel, such techniques are either already in use or have demonstrated feasibility for near term implementation. It is recognized that the simplest of these systems are presently limited to periods of about one week for unattended operation. It was felt, however, that in a fairly short time, minimum efforts at improvement and imaginative packaging could result in being able to extend time for field use as well as extend this technology to more complex operations.

It is Recommended that:

(a) a lead agency role be accepted by EPA to promote and carry out additional efforts toward development of small automated wet chemical systems for the measurement of total dissolved phosphorus, nitrogen compounds, and dissolved and total organic carbon.

6. Additional technologies that have been specifically identified as having high potential for successful development in the next few years are acoustic echo sounding and optical techniques as applied to suspended particulate measurements, and atomic absorption spectrophotometry; neutron activation, and energy dispersive X-ray spectroscopy for metal detection. Further evaluation is required however, before assessment of the most effective technique for in situ sensing can be made.

It is Recommended that:

(a) on-going efforts involving the optical measurement of suspended particulates be accelerated and expanded to include existing expertise, particularly that within NASA,

(b) NOAA serves as the lead agency to further evaluate existing metal ion measurement systems and accelerate development of in situ sensors,

(c) additional funding to support these areas be secured through elevating their priorities within agency programs and through interagency agreements for sharing research and development costs.

7. All sensor technology panels, regardless of the technology specialty being considered, stressed the need for improved sensor cleaning and anti-fouling techniques. The performance of any sensor that must operate unattended in a natural water environment is greatly degraded by the presence of sand, sediment and biological organisms.

It is Recommended that:

(a) additional efforts be directed toward development of cleaning techniques and prevention of fouling for unattended automatic sensors in natural water environments.

8. Although the workshop focused on development of systems applicable to point type measurements, it was recognized that there is also a need for mesoscale measurement schemes to obtain synoptic data over large areas and to acquire large scale information such as total flow in streams and oil spill coverage.

It is Recommended that:

(a) consideration be given to design or systems to obtain large scale measurements.

WATER QUALITY SENSOR WORKSHOP

February 14-16, 1978
Las Vegas, Nevada

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WORKSHOP AGENDA

WATER QUALITY SENSOR WORKSHOP
(With particular consideration to in situ small waterborne system deployment)

Cochairmen - John D. Koutsandreas
Donald T. Wruble

TUESDAY, February 14, 1978

0800 - 0900	Registration & Get-Acquainted Coffee	
	INTRODUCTORY SESSION	
0900 - 0905	Call to Order	Mr. Donald T. Wruble
0905 - 0910	Welcome	Mr. George B. Morgan
0910 - 0930	Keynote	Dr. Richard M. Dowd
0930 - 0935	Introductory Remarks	Dr. Richard W. Paulson
0935 - 0945	Workshop Schedule, Logistics, Plans, Procedures	Mr. Donald T. Wruble
0945 - 0955	Break	
	AGENCY PROGRAM PRESENTATIONS	
0955 - 1005	Overview	Mr. John D. Koutsandreas
1005 - 1030	EPA	Mr. Tom Murray
1030 - 1055	NOAA	Ms. Barbara Pijanowski
1055 - 1120	Department of Energy	Dr. Mary S. Hunt
1120 - 1145	Corps of Engineers	Mr. Earl Eiker
1145 - 115	Lunch	
115 - 140	NASA	Mr. Nelson Milder
140 - 205	National Bureau of Standards	Dr. William H. Kirchoff
205 - 230	Department of Defense (Navy)	Mr. Thomas Harris
230 - 250	Break	
250 - 315	U.S. Coast Guard	Lt. Cmdr. Vincent DiPasqua
315 - 340	U.S. Geological Survey	Dr. Richard W. Paulson
340 - 405	U.S Dept. of Agriculture	Dr. Frank Scheibe
405 - 430	Participant Comments/ Observations	Open Discussion

WEDNESDAY, February 15, 1978

SPECIAL GUESTS

0830 - 0855	Sensor Needs in EPA Regional, State & Local Operational Monitoring Programs	Mr. Clifford Risley
0855 - 0930	Water Quality Sensor R&D in Canada-Canada Center for Inland Waters	Dr. Kenneth Birch

UNIVERSITY PRESENTATIONS (New Technology)

0930 - 0950	University of Wisconsin	Dr. W. T. Blaedel
0950 - 1010	Break	
1010 - 1035	University of Texas A&M	Dr. Richard Newton
1035 - 1100	University of Michigan	Dr. K. H. Mancy
1100 - 1125	Louisiana State University	Dr. Charles Whitehurst
1125 - 1150	University of Florida	Dr. Roger G. Bates
1150 - 1215	University of Rhode Island	Dr. F. H. Middleton
	LUNCH	

PANEL SESSIONS

130 - 145	Panel Assignments & Instructions
145 - 500	Panels - 1st Session

THURSDAY, February 16, 1978

0830 - 1200	Panels - 2nd Session	
	LUNCH	
130 - 250	Report Preparation	
250 - 300	BREAK	
300 - 400	Panel Report Presentations	
400 - 425	Report Discussion/Comments	
425 - 430	Concluding Remarks	Mr. John Koutsandreas

FRIDAY, February 17, 1978 - (Panel Chairmen only)

Workshop Report Finalization